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PHOTO-CHEMISTRY

BY

S. E. SHEPPARD, D.Sc. (Lond.)

FORMERLY 1851 EXHIBITION RESEARCH SCHOLAR OF UNIVERSITY COLLEGE, LONDON

WITH ILLUSTRATIONS AND FIGURES

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PREFACE

In the following pages I have endeavoured to present a connected, and, in a measure, continuous account of the subject of photo-chemistry in its modern development. Unification of the scattered elements of this subject is no easy task, in view of the almost inevitable contingency of actino-chemical changes with other thereby recognized and characterized alterations of material systems.

There has resulted a delay, not without danger, in the attainment of independent status by photo-chemistry, having been for so long ancillary to her elder sisters, thermo- and electro-chemistry, so that only by a masquerade, momentous both for theory and practice, as the science of radio-activity has this Cinderella of the sciences been accorded its due recognition.

There exists, and is likely to continue, some difference of opinion as to the desirability of incorporating a discussion of photo-physical and radiation phenomena and laws in a work on photo-chemistry. But neglect of this aspect of the question and too narrow a circumscription of its domain can only lead to further delay in the discrimination of a definite body of laws for this science. For this reason the plan has been followed in the present work of discussing at some length certain intensive studies on cardinal points in photo-chemical change rather than that of enumerating and recording every example of photo-chemical reaction or light-sensitive substance. The aim has been to aid students with examples of working hypotheses helpful in the completer investigation of the economy of any given photo-chemical reaction.

As such a working hypothesis, the conception that in

photo-chemical change singular intermediate complex ions, or, specifically speaking, veritable latent light-images, are formed, appears the most promising. The *singularity* involves concordance of the reaction order or kinetics of their growth and decay with the optical conditions of absorption and emission, the *intermediacy* or metastability of their constitution implies imperfect coincidence of photo-chemical equilibrium with the thermodynamically stable equilibria possible to the independent chemical components present.

Every photo-chemical change is in consequence virtually photographic, the equilibrium to which it tends implies, so to say, a radiation proto-type of a colloid, a characteristic organization radiating from a centre, as the *unit* effect possible. So long as the action is in agreement with the principle of virtual velocities, the change is reversible, the partial chemical transformations tautomeric in type. But any acceleration of the temps of the change involves a loosening of residual affinities in the group which may readily lead to an irreversible transfer of an electron to a depolarizer and consequently to a *per saltum* mutation of the total energy such as the quantum theory of Planck demands. Hence the maximum work developable is as much contingent on the accommodation in space and time of a mutable depolarizer as on the nature of the system insolated, a point emphasized by Grotthus and recently reiterated by Prof. Bancroft. On this view the primary or direct photo-chemical change may well be termed catastrophic, and it is only by its coupling with a depolarizer and development as an indirect action that the discontinuous nature of the change is masked by a slow evolutionary process. It is hoped that the references given, although not intended to form a complete index to the literature, will serve as guides to the main sections of this. The abbreviations adopted are in most cases those employed by the Chemical Society in their *Journal*. Thanks are due to this Society for permission to use Figure *34* taken from their *Transactions*. In regard to the photo-physical part of the initial chapters I am indebted directly and personally, as well as indirectly through his writings, to Prof. Karl Schaum,

editor of the *Zeitschrift f. wissenschaftliche Photographie, Photochemie, u. Photophysik.* For invaluable assistance in the section dealing with the physics of photo-electric effects, phosphorescence, and fluorescence, my thanks are due to my friend, Dr. E. N. da C. Andrade, whilst I desire to record my indebtedness also to Messrs. C. E. K. Mees, Cr. Winther, F. Weigert, and others, for valuable and chastening criticism.

Lastly, I wish to acknowledge the sustained interest and guidance afforded by Sir William Ramsay throughout the progress of the work in MS. and in proof.

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PHOTO-CHEMISTRY

CHAPTER I

HISTORICAL

The early history of photo-chemistry is so bound up with the progress of science in general that much discussion of it apart would hardly be profitable. The intuitive knowledge which the ancients possessed of light and its operations was extremely deep; it was, however, synthetic and expressed in their art. It has been well remarked of the Greeks that their metaphysic was a profoundly organized science, but their science a confused metaphysic. Hence we find their views, as transmitted to us, on the nature of light, distinguished by a naïve realism, which laid more emphasis on the psychological aspect of vision than on the outer co-ordination of things seen.

§ 1. Three Theories of Light.

The emissive theory of Plato supposed that the interference of a flux from the eye with a kindred flux from a source of light constituted the datum of sense, a visual appearance. The second condition was wanting in darkness, and so, the circuital condition not being fulfilled, nothing was seen. However crude the doctrine of ocular beams may seem, it has the merit of taking into consideration the reciprocal relation of subject and object; modern physiology has restated Plato's hypothesis in the form, that percipience and the direction of attention are correlated to an efferent nerve-current.

Whilst Plato does not specify the carriers of his "streams

of light," Lucretius and others held a quasi-tactile theory as to the action of vision, regarding the ocular beams as species of levers by which the eye felt or "palped" the object. On the other hand, Pythagoras supposed that vision was excited by small particles emitted by visible objects.

Opposed to these views of light as a primary quality was the opinion of Aristotle, who considered that light was not a substance in any sense, but a peculiar quality or action (energeia) of a pellucid medium, which intervened between the object and the eye. Colour was a minor, light a major activation of this medium.

These three theories, the *normative* theory of Plato, the *corpuscular* of Pythagoras, and the *undulatory* of Aristotle, occur in one form or another in all subsequent speculation.

§ 2. Alchemists and Iatro-chemists.

The alchemists, preoccupied with the endeavour to isolate the assumed abstract principles or qualities of material substances, with the aim of transmuting metals, seem to have paid little practical attention to the action of light. Similarly with the iatro-chemists, who by liberal experiment on the human frame, founded rational therapeutics, naturally breaking many eggs in preparing their omelette. And as to the alchemists, their dialect or jargon differed from ours, but as Berthelot remarks[1]: "Les opinions auxquelles les savants tendent à revenir aujourd'hui sur la constitution de la matière ne sont pas sans quelque analogie avec les vues profondes des premiers alchimistes."

§ 3. Observations on the Chemical Action of Light.

The influence of light on the formation of the green colour of plants, and the converse bleaching in darkness, was noted by Aristotle (350 B.C.); and Vitruvius remarked on the bleaching of pigments by light (100 B.C.). The writings of the

[1] M. Berthelot, *Les Origines de l'Alchimie*, Préface, p. 15. Paris (Steinheil), 1885.

alchemists are full of references to the action of light, but couched in such vague and mystic terms that it is uncertain whether the connotation is abstract or concrete. It is with the end of the seventeenth century that really empirical study begins. Ray, the botanist, distinguished the action of light from that of air in plant growth. The Prussian Chancellor, Bestucheff, the discoverer of "iron tincture," or "golden drops," a solution of ferric chloride in alcohol, noticed that the colour was discharged in sunlight but recovered to some extent in darkness, so that he may be credited with the discovery of the reversibility of photo-chemical action.

§ 4. Chemical Production of Light.

The investigation of phosphorescent bodies (Baldwin's phosphor = fused calcium nitrate), and the subsequent discovery by Brand (1675) of phosphorus, represent the first phase of this side of the subject. Indirectly they led to the first notice of the light-sensitiveness of silver salts (J. H. Schultze, Professor of Medicine at Altdorf, 1727),[1] which remained, however, unremarked. Priestley[2] supported the emission corpuscular view of light, as explaining best the slower changes of colour of bodies exposed to light.

Of greater importance for our particular phase of chemistry were the experiments of Scheele (1777).[3] He defined a large number of photo-chemical reactions, in especial the blackening of silver chloride in light and the separation of chlorine. He was also the first to use the spectrum photo-chemically, remarking that "horn-silver"[4] became black in the violet rays first, which he attributed to the greater readiness with which these parted with phlogiston.

Of other experiments in the last quarter of the eighteenth

[1] See J. M. Eder, *Phot. Corresp.*, 1881, p. 18.

[2] *History and Present State of Discoveries relating to Vision, Light, and Colours*, 1777.

[3] *Aëris atque ignis examen chemicum.* Upsala et Leps., 1777.

[4] Fused silver chloride.

century, Senebier's[1] are the most interesting. He noted that alcoholic tinctures of plant pigments, such as chlorophyll, were bleached by light, especially in the presence of air. Berthollet (1785), the prophet of the mass law of chemical action, noted the decomposition of water by chlorine in sunlight.[2] This discovery led some eleven years later to the construction of the first chemical photometer or actinometer by de Saussure.[3] The latter also employed actinometers made from paper soaked in vegetable extracts, which he employed in his meteorological observations in the High Alps. This bleaching action was attributed by Berthollet to an absorption of oxygen, set free by light. The "Essay on Combustion," by Mrs. Fulhame (1794), deserves mention, since she insisted on the presence of water as a necessary condition for the reduction of metals from their salts by light. This latter she considered as similar in its chemical behaviour to carbon, sulphur, and hydrogen, and only reacting by mediate decomposition of water.

§ 5. Substantial Theory of Light.

Light was classed at this period among the imponderable substances, with heat and electricity. Thus Davy (1799) considered that light combined with oxygen to form oxides, oxygen gas being a direct compound of the stuff—*light*, and oxygen potential.

§ 6. Infra-red and Ultra-violet Rays.

In 1800 W. Herschel made the capital discovery of the infra-red region of the spectrum, and Ritter (1801) noticed the action of the ultra-violet rays upon silver chloride.

In 1802 Wedgwood and Davy were taking photographs on paper treated with silver salts, but could not fix them.

[1] J. Senebier, *Mémoires physico-chimiques sur l'influence de la lumière.* Geneva, 1782.

[2] *Histoire de l'Académie Royale des Sciences de Paris*, 1785, p. 290.

[3] Crell's *Chem. Ann.*, 1796, I. 356.

Thomas Young, the reviver of the undulatory theory (1801–1803), showed by projection of Newton's rings on silver paper that the ultra-violet rings behaved similarly to the visual. J. B. Seebeck showed that silver chloride could to some extent reproduce the spectrum, especially after an initial exposure.[1]

§ 7. Chlorine Reactions.

Gay Lussac and Thénard (1809–1810) discovered the influence of light on chlorine and hydrogen, and on chlorine and ethylene. They considered that light acted similarly to heat. Davy opposed this by citing the great chemical activity of the violet and ultra-violet, where the heating effect is small. In 1812 he discovered the photo-chemical synthesis of CO and Cl_2 to phosgene gas. Davy also gave prominence to the view that the more refrangible rays exert a reducing, the less refrangible an oxidizing, action. In his researches on iodine he noted a darkening of silver iodide in light. Steffens recorded an opposite result. It is known now that the darkening only takes place in presence of excess of silver nitrate.

§ 8. Salts of Metals.

The light-sensitiveness of a variety of other salts of metals ($HgCl_2$ + ammonium oxalate, Planché[2]; manganese salts, by Brandenburg[3]) continued to be noticed. Before detailing further instances, it is necessary to refer to the important work of Grotthus.

§ 9. The Absorption Law.[4]

Grotthus (1818) endeavoured to combine the known facts into a body of generalizations, based on the electro-chemical

[1] Eder's *Gesch. d. Phot.*, Bd. I., 3 Auf., 1905.

[2] *Journ. de Pharm.*, 1815, p. 49.

[3] *Jour. f. Chem. u. Phys.*, 1815, **15**, 348.

[4] Gilbert's *Ann. d. Phys.*, **61**, 50 (1819); see also W. Bancroft, *Journ. Phys. Chem.*, **12**, 213 (1908).

theory of Davy and Berzelius. The most important of these is generally known as the *photo-chemical absorption law.*

"Only the rays absorbed are effective in producing chemical change."

Considering that light consisted of + and − electricity travelling side by side, as ± E, he assumed that photo-chemical change was equivalent to a direct electrolysis, the components separated combining with + and − electricity of light. He propounded four main classes of action.[1]

I. The initial action of light upon a salt in solution was to dissociate this salt into products; one part being much *less* soluble than the original salt, the other much *more.* For example, a basic salt is precipitated from a solution of stannous chloride in water covered with oil, very much more rapidly in light. A similar effect is obtained for mercuric chloride mixed with ammonium oxalate, which precipitates calomel, and for a solution of ferric oxalate, which precipitates ferrous oxalate. The *more* soluble resultant is, apparently, in Grotthus' opinion, the acid component which is liberated.

II. In oxygen or chlorine compounds decomposed by light, the light deoxidizes or dechlorinates the electropositive (usually solid) constituents, or prevents their oxidation, etc.; *in either case* exerting the *inverse* action on the inert, electro-negative substance (usually liquid or gaseous),[2] also upon its own imponderables ± E. But also out of this first ponderable compound, continued light action may remove the more remote constituents according to the same law, especially with the aid of water. The action will not terminate until the light has brought about the most complete separation of the ponderable substances, and has made new compounds of the same with its own imponderable elements (± E). He further points out that oxidation, hydrolysis, chlorination, etc., always imply simultaneous deoxidation, etc., elsewhere. Ponderable and imponderable substances are, in his view, really only relative,

[1] Ostwald's *Klassiker*, **152**, 94.

[2] It is important to note that Grotthus thus implies the possibility of change in *polarization* of light, without a significant chemical change, on contact of radiation and matter.

and usually refer to those changes which the ponderable matter undergoes. "A ray of light is therefore a line along which the elements of neutral electricity arrange themselves in polar fashion. There is no actual separation involved, but only the tendency to the separation,[1] and to alternating molecular recombination of the same." Further details of Grotthus' generalizations must be studied in the works cited. In its remarkable prevision of the electro-chemical nature of light, Grotthus was much in advance of his time. The conception of light as a continuous current has not proved a sufficient explanation; it has rather to be regarded in particular cases as a polyphase alternating current.

§ 10. Photo-chemistry up to Bunsen and Roscoe.

From this time onwards increasing numbers of photo-chemical reactions were recorded. Many experiments and descriptions of an uncritical nature might be mentioned dealing with the behaviour of organic substances in light, but space forbids. Chevreul (1837) published an important work on vegetable colours, in which the influence of air and moisture in assisting bleaching was emphasized. An important period begins with the researches of N. de Niépce and Daguerre (1814–1830),[2] which, as is well known, resulted in the first practical photographic process. At one time, the chemical effects of light were supposed to be due to a particular class of rays, but experiment has confirmed Grotthus' principle, re-emphasized by Draper (1839), that *absorption* is the determinative factor. Biot[3] and Malaguti[4] noticed that many transparent substances could greatly reduce photo-chemical effect; and this was adduced as proof of the retention of chemical rays. Actually, the rays retained are ultra-violet, which are the most productive of chemical reactions. E. Becquerel,[5] one of the

[1] What would now be termed "potential."

[2] Cf. J. M. Eder, *Gesch. d. Photograph* (153–208), and J. Werge, *Evolution of Photography*. London, 1890.

[3] *C. R.*, **8**, 259, 315.

[4] *Ann. Chim. et Phys.*, **72**, 5 (1839).

[5] *Ibid.* [3] **9**, 263 (1843).

greatest names in photo-chemistry, observed a differential behaviour of silver chloride to the spectrum, which, in connection with phototropy and chromatic adaptation, will be noticed later. It is now known that by suitable modification of the receiving substance, every radiation can exert chemical action. A great practical step in this direction was made by H. W. Vogel (1873), who showed that by suitably incorporating colouring matters with silver salts they could be made sensitive to green and yellow light.

We must note at this point a theory advocated by Ritter, Herschel, and Becquerel,[1] viz. that the short waves of great refrangibility exert a *reducing* action, as opposed to the *oxidizing* action of the longer waves of greater refrangibility. This theory, which was also maintained by Draper, is of fundamental moment for the interpretation of photo-chemical phenomena, but requires careful handling in particular cases.

The number of substances specifically sensitive to light continues to increase, and many will be referred to in the course of this book. The year 1854 saw the commencement of the actinometric researches of Bunsen and Roscoe, which have remained a model for all subsequent research on the dynamics of photo-chemistry.

[1] *La lumière, ses causes et ses effets*, 1872.

CHAPTER II

THE MEASUREMENT OF LIGHT-QUANTITIES

§ 11. Geometrical Laws.

There are certain fundamental laws of geometrical optics which are involved in all quantitative light-measurements. But it is necessary to remember that in geometrical optics no special concept as to the nature of light is made ; this becomes necessary in discussing the physical interaction of light and material bodies, and then these empirical laws appear at the most as comprehensive approximations or simplifications under certain narrowed conditions. These laws are—

I. *Light is propagated in straight lines*, which is easily deduced from the nature of the shadows thrown by a small light source.

II. *The rays in a bundle are mutually independent*, or the effect of a bundle of rays is simply that due to their sum.

Thus the light-action on a screen produced by a luminous body shining through a hole of moderate dimensions is simply proportionately lessened as the size of this hole is diminished. Both of the above laws cease to hold when the hole becomes very small ; in this case the phenomena of diffraction and interference come into observation.[1] It should be remembered that rays are only a convenient expression for the paths of transference of energy and have no real physical existence. We cannot isolate a light-ray, since the smaller we make the bundle of rays, by narrowing a hole, for example, through which light is streaming the less the property of straight-line transference is preserved.

[1] Cf. E. C. C. Baly, *Spectroscopy*, this series, p. 16.

If light-rays are stopped by any object, we get the phenomena of reflection and refraction. The incident light-ray is split into two parts, one continuing a deviated course through the new medium, the other being returned into the first medium.

III. *All three rays lie in the same plane.*

IV. *The incident and reflected rays make the same angle with the normal to the new surface.*[1]

V. *The angle of refraction is related to the angle of incidence by the equation* $\mu = \frac{\sin\theta}{\sin\theta'}$. θ and θ' being the angles between the normal and the incident and deviated rays respectively. The constant μ is termed the refractive index of the body with regard to the surrounding medium. For definite colour or wave-length μ is a natural constant; refractive indices are usually given with respect to air or vacuum. Further, we know, from Newton's fundamental experiment, that white light is a manifold of various qualities or species. The refractive index usually increases from red to blue, and upon this depends the decomposition of white light by a prism. This property of transparent bodies is known as their dispersion-power.

The Law of Fermat.—This law, sometimes termed the principle of a characteristic optical path, sums up the foregoing experimental facts of the propagation of light in the conception that a properly defined optical path of principal importance, *e.g.* of the "Hauptstrahl" or principal ray in an optical system, is sufficiently defined by the vanishing of the first variation of the sum of the products of the refractive indices of the media, taken consecutively, and the length of path traversed in each. Suppose a ray of light to pass from a point P by any number of refractions and reflections to another point P', then the sum of the products of the refractive index of each medium into the distance traversed, say $\Sigma\mu l$, is an

[1] The reflection dealt with above is "regular" reflection at a definite geometrical surface. In "diffuse" reflection, which will be noted under photometry, light is reflected in all directions; this is due to the irregularity of the surface, which consists of an infinite number of smaller surfaces inclined at all angles.

extreme value,[1] that is, it differs from the corresponding sum for all paths infinitesimally remote from it in reality, by quantities of the second order at the most. Suppose a variation of the first order be denoted by prefixing the symbol δ to any optical path, then

$$\delta \Sigma \mu l = 0$$

The product of the refractive index with the distance traversed in any homogeneous medium is termed the optical path or optical length of a ray.

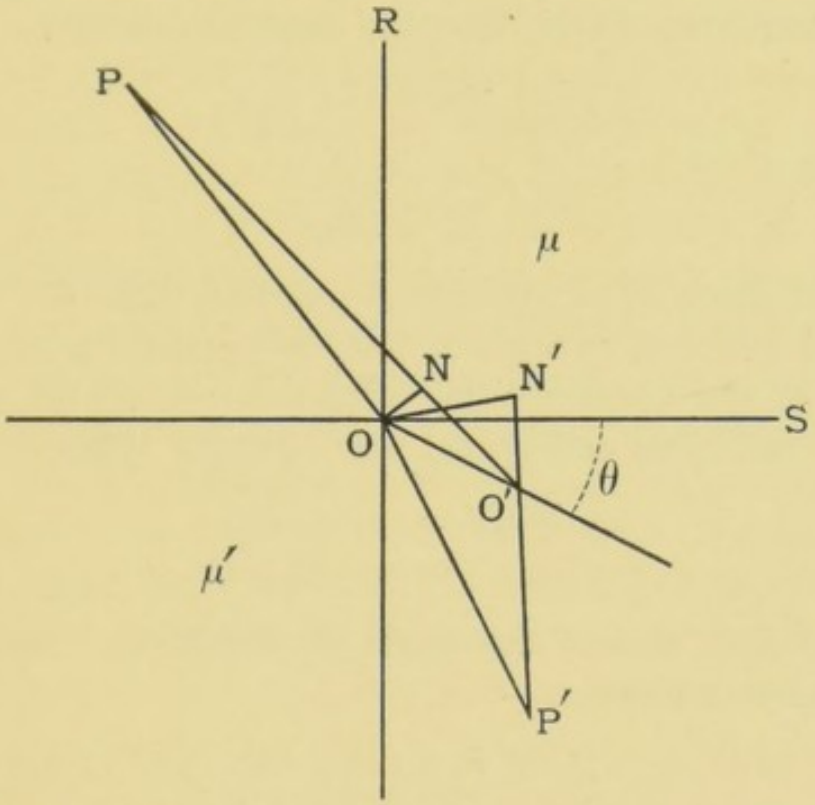


FIG. 1.

The principle is easily proved for single refraction. Let POP′ (Fig. 1) be the path of the ray, OS be the section of the plane of incidence POR with the bounding surface or tangent plane of the second medium. Suppose O′ be a point only infinitesimally remote from O in the surface of the refracting medium, and let OO′ enclose an angle θ with the plane of incidence, that is, with the line OS. Drop a perpendicular ON from O on to PO′ and another ON′ on to P′O′,

[1] Sometimes simply abbreviated to an "extremal" in dealing with the general problem of the variation of an integral.

so that $PO' = PO + NO'$, $O'P = OP' - O'N'$, with sufficient approximation, *i.e.* so that the squares of differences are negligible. Then, with the same degree of approximation,

$$NO' = OO' \cdot \cos POO' ; \; O'N' = OO' \cdot \cos P'OO'$$

In order to calculate cos POO', let the direction-cosines of the lines PO and OO' be described with respect to a pair of rectangular axes, so that we have the directing lines OR, OS, and OK, where OK is supposed perpendicular to the plane of the paper, and must be supplied in imagination. Call ϕ the angle of incidence PON, then the direction-cosines of PO are

$$PO : \cos \phi, \sin \phi, o$$

and those of OO'

$$OO' \quad o, \cos \theta, \sin \theta$$

It is a theorem of analytical geometry that the cosine of any angle between two given lines is equal to the sum of the products of the corresponding direction-cosines of the same lines referred to an orthogonal pair of axes. Hence—

$$\cos POO' = \sin \phi \cdot \cos \theta$$
$$\cos P'OO' = \sin \phi', \cos \theta$$

supposing ϕ' to denote the angle of refraction. Hence, from the preceding equations—

$$\mu \cdot PO' + \mu' \cdot O'P' = \mu \cdot PO + \mu \cdot OO' \cdot \sin \phi$$
$$\cos \theta + \mu' \cdot OP' - \mu' \cdot OO' \sin \phi' \cdot \cos \theta$$

But we have from the definition of the refractive index the relation—

$$\mu \cdot \sin \phi = \mu' \cdot \sin \phi'$$

hence, provided the point O be infinitely near to the point O',

$$\mu \cdot PO + \mu' \cdot OP' = \mu \cdot PO' + \mu' \cdot O'P'$$

exclusive of fractions of the second or higher order, which proves the theorem for a single refraction. The proof for a single reflection is relatively simpler.[1] The vanishing of the

[1] See P. Drude, *Lehrb. d. Optik.*, p. 10. S. Hirzel, Leipzig (1900).

first variation of an analytic function may correspond either to a maximum or a minimum of the argument. In the case when the refracting boundary is a true plane, it follows from the construction given that for both refraction and reflection the actual optical path is a minimum. The principle is therefore often denominated the theorem of the shortest optical path. But it must be remembered that in the case of *curved* surfaces, it depends entirely on the nature of the curvature as to whether the optical path is a maximum or minimum.

As the refractive-index is inversely proportional, on the wave-theory of light, to the velocity of propagation of light, it follows that the optical path μl is proportional to the time taken by the light to traverse the distance l. Hence the principle of the shortest optical path coincides with Fermat's principle of the quickest transit of light, always provided that there be no such curvatures interposed as make the time of transit a maximum. On the principle of the super-position of variations, the equation $\delta\Sigma\mu l = 0$ found for one reflection or refraction can be extended to the case of any given number. If the equation be written in the form $\int \mu dl =$ maximum or minimum, and the corresponding reciprocal of the velocity of propagation be substituted for μ, we have the equation for the time of transit—

$$\Delta t = t - t' = \int \frac{dl}{V} \text{ is a maximum or a minimum.}$$

§ 12. Refractive Indices of Metals and Absorbing Substances.

It is important to notice that for metals, for colloid metal solutions, for dye-stuffs, and generally for all cases where there is a strong and selective absorption of light, the refractive index μ, or the specific refractivity R_n, where n is the vibration-frequency of a monochromatic ray, is complex, that is to say, it is interdependently variable with the specific

absorption of the substance for light. As a first approximation it may be written—

$$R_n = r_n(1 - i \cdot \kappa)$$

where r_n is the ordinary refractivity for supposed minimum absorption, and κ is the absorption index, which is a function of the wave-length or vibration-frequency of light (*vide* p. 136). The symbol $i = \sqrt{-1}$, and is not the symbol of a numerical quantity but of an operation.[1] The relation of the refractivity and dispersion of light by media to their chemical constitution and to the dynamics of the absorption of light is discussed later.

§ 13. Photometry.

On considering a chemical system acted on by light, it is evident that the extent and progress of the action will depend on a large number of purely physical factors, some peculiar to light as a phenomenon independent of physical bodies, others depending on its interaction with these. We require to know (*a*) the amount of energy radiated in relation to the nature, size, form, etc., of the source; (*b*) the light-energy incident on the chemical system, which, again, depends on such factors as its position, its reflecting power, and so forth; (*c*) the energy transmitted. Now, from what has already been said, it is obvious that we can make measurements of the radiated energy in three ways.

I. As light, by physiological action.

II. As heat, by which we can measure the total energy.

III. By chemical action.

These three methods correspond to the titles (I.) Photometry, (II.) Radiometry, (III.) Actinometry.

Now, as far as the physical factors indicated above are concerned, the laws are the same, and all the conditions are equally applicable, although they were historically derived by the methods of photometry in the narrow sense. We shall now briefly consider the more important relations, and the

[1] Algebraical expressions in which the symbol $\sqrt{-1}$ occurs are termed "imaginary" or "absurd" quantities. Cf. A. N. Whitehead, *An Introduction to Mathematics* (Williams and Norgate, 1911).

definitions of the quantities involved. We cannot deal absolutely with the energy radiated without at the same time considering the recipient surface. Further, in considering the three methods of measurement, it is to be noted that the eye cannot make absolute judgments of the amounts of light radiated by different sources. But if two surfaces which are separately illuminated are made optically contiguous, then the eye can distinguish very small differences in the brightness of the surfaces. On this faculty depends the methods of photometry, which are essentially comparative. Brightness is a subjective quality, expressing simply the degree of the physiological stimulus due to light, which has of course its objective correlative in the "photo-chemical effect," whatsoever that may be, in the retina.

Light-Sources.—All self-luminous bodies and also diffuse reflectors may be considered as light-sources proper. They may vary in size, in intensity, and in quality or colour of the light emitted. The ideal light-source, for simplicity of treatment, is a point, a good approximation to which is obtained by a hole pierced in a screen illuminated by a convenient source.[1] The conditions of experimental work will determine how far any light-source may be treated as a point-source.

Amount of Light.—Considering such an ideal point-source in free space, then the amount of light emitted is that which falls on a surface completely surrounding it. This we term A.

Light-Strength.—A useful conception is that of a tube of light. This is a cone of rays whose apex is the point-source, and the ideal bounding walls of which are formed by light-rays. In every cross-section of this tube or cone the amount of light will be constant. This follows immediately, for a perfectly transparent medium, if we consider that the amount of light is the energy transmitted per unit time through the cross-section of the tube. If we consider a sphere surrounding the point as centre at a radius of 1 cm., the cone will cut off a surface, ϕ, on this, the angle subtended by the cone.

[1] Compare this use in Young's celebrated experiment on interference. Preston, *Theory of Light*, 2nd ed., p. 24; Baly, *Spectroscopy*, p. 16.

Taking a unit cone subtending $d\phi$ on the sphere, the amount of light will be proportional to $d\phi$, or—

$$d\Lambda = \mathrm{I}d\phi$$

I is called the intensity or illuminating power of the point-source in the direction of the axis of the cone. Physically, it is the amount of light radiated by the source on to unit surface at unit distance, the surface being normal to the rays. If I is independent of the direction of the rays, the total amount of light, Λ, will be equal to the sum of that due to all unit cones emergent from the point; or, since 4π is the total angle subtended at unit distance—

$$\Lambda = 4\pi\mathrm{I}$$

Generally $\int \mathrm{I}d\phi = \Lambda$

From this the mean intensity or light-strength—

$$\mathrm{I}_m = \frac{\Lambda}{4\pi}$$

Intensity of Illumination.—This is the amount of light received by unit surface. It depends on the distance of the illuminant and the inclination of the surface to the direction of the rays. Keeping still to point-sources, we have the following laws of illumination.

The Inverse-Square Law.—As before, light is radiated from a point as centre on to a sphere. On a surface element, ds, of sphere radius 1, there falls the amount of light $\mathrm{I}ds$. Hence, on an equal surface element of a sphere at radius r $\frac{\mathrm{I}ds}{r^2}$ will fall, since the total surface, receiving still the *same* amount of light at distance r, is r^2, the surface at radius 1. Hence the illumination is inversely as the square of the distance from the source. Now, for a surface conceived as consisting of a number of such point-sources, with intensities I_1, I_2, etc., at distances r_1, r_2, etc., from an illuminated point, the amount of light received by this will be—

$$\Lambda = \frac{a_1\mathrm{I}_1}{r_1^2} + \frac{a_2\mathrm{I}_2}{r_2^2} \ldots$$

If the point be at such a distance that the differences $(r_1 - r_2)^2 \ldots$ are negligible—

then $$\Lambda = \frac{a_1 I_1 + a_2 I_2}{r^2} + \ldots$$

So we can apply the inverse-square law for a surface at a sufficiently great distance.

Intensity of Illumination (*continued*).—*The Cosine Law.*—Suppose the unit cone of angle $d\phi$ cut off ds from any surface intercepting it, and let the normal to ds make the angle θ with the axis of the cone. Let r be the distance of ds from the point-source—

then $$d\phi \cdot r^2 = ds \cos\theta$$

But $$d\phi = \frac{d\Lambda}{I}$$

Hence the amount of light falling on ds, the unit surface—

$$= \frac{I ds \cos\theta}{r^2}$$

Considering unit surface, $ds = 1$, the amount of light falling on *unit* surface, say—

$$I' = \frac{I \cos\theta}{r^2}$$

Hence, the *intensity of illumination* of a surface lit by a point-source is proportional to the specific intensity of the light-source, inversely proportional to the square of its distance, and proportional to the cosine of the angle which the normal to the surface makes with the direction of the light-rays.

The Complete Photometric Law.—The condition that the light source shall be a point is not always realizable. Obviously the illuminating power of a source, and hence its photometric or photo-chemical effect will depend upon the area of its surface, its specific intensity, and its inclination. The following construction shows the relation (see Fig. 2) :—

Let AC, BC be parallel rays from the surface AB, making an $\angle\ \psi$ with the normal to AB. Then the action of AB in the

direction of AC, BC will be the same as that of its projection, a surface AB′, normal to AC, BC. Hence the illuminating power is proportional to AB′ or AB cos ψ. Writing for AB′

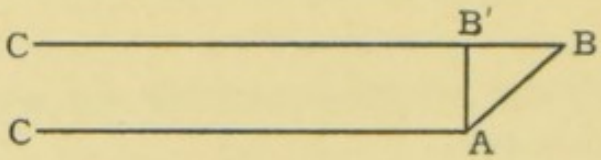


FIG. 2.

the surface element dS, and I for the specific intensity of the light-source in the direction normal to its surface, then Ids cos ψ is the light-strength or intensity in the given direction. This is the so-called "cosine law" of emission of Lambert.[1]

From this and from the foregoing, it follows that the light falling on a surface element ds' from a surface element ds of a light-source is given by

$$I' = \frac{I ds' ds \cos\theta \cos\psi}{r^2}$$

For unit areas this becomes

$$I' = \frac{I \cos\theta \cos\psi}{r^2}$$

where I is the specific intensity or illuminating power of the light-source for unit area, and I′ is the intensity of illumination. This expression gives the complete law of photometry, but in practice the conditions are arranged for right-angled radiation, so that the cosine factor vanishes.[2]

Albedo.—The amount of light reflected in every direction by a diffusely reflecting surface on direct normal illumination was termed by Lambert its albedo. For a complete reflector the albedo = 1. It is a factor of importance in photography, but the values are only known for a few surfaces. For snow,

[1] H. Lambert, *Photometria, sive de mensura et gradibus colorum et umbrae* (1760); also Ostwald's *Klassiker*, Nos. 31, 32 (Leipzig).

[2] For a rigid derivation of Lambert's law, see Lommel, *Wied. Ann.*, **10**, 449 (1880). For self-luminous bodies the law was experimentally confirmed by Möller, *Wied. Ann.*, **24**, 266 (1885). Its validity for radiant heat was established by H. Wright, Drude's *Ann.*, **1**, 17 (1900).

H. W. Vogel gives 0·783, Zöllner for white paper 0·7, but this must vary, obviously, with the paper. Lambert's law is usually assumed for good diffusely reflecting bodies, but actually considerable deviations are found, and the relation for other than normal incidence is very complicated.[1] Wright succeeding in obtaining very good diffuse reflectors (*i.e.* showing little or no regular reflection) by compressing powders. He found that when α is the angle of emission, β the angle of incidence, then for constant β, the Lambert cosine law holds, but for constant α, the radiation is not proportional to cos β.

§ 14. Experimental Photometry.

Practical photometry depends on judging when two surfaces are equally bright, *i.e.* equally illuminated. Beside measurements of the intensity or light strength in a given direction, it may be desired to measure the total amount of light radiated, or light-stream, and the mean light strength (*vide* p. 77). For details as to the calculation of these and for special cases of illumination by different commercial light-sources, the reader is referred to standard works on photometry.[2] In addition, an important application for photo-chemistry is the photometry of absorptions, which, together with the laws of absorption of light is dealt with subsequently.

Light Units.—Photometry being comparative, it is necessary to have a definite unit or standard. This has long been a vexed question, and is by no means settled yet. The requirements of a primary standard are that it shall have an exactly reproducible value at all times and places, and keep to that value over a sufficient time for the comparison measurements. At present, various standards are still in use in different countries. Light-sources of constant and determinable

[1] E. V. Lommel, *Wied. Ann.*, **36**, 473 (1889); H. Seeliger, *Vierteljahrschr. d. Astronom. Ges.*, **21**, 216 (1886).

[2] For example, A. Palaz, *Photometry, a Treatise for Industrial Purposes*, trans. from the French by Patterson (Sampson, Low, Marston & Co.). Further, *Lichtstrahlung und Beleuchtung*, Paul Högner (8, Hft. of Electrotechnik in Einzeldarstellung) (F. Vieweg, Brunswick, 1906).

value will be dealt with later in connection with actinometry and the experimental conditions of photo-chemical investigations.

In England the former standard was the Parliamentary

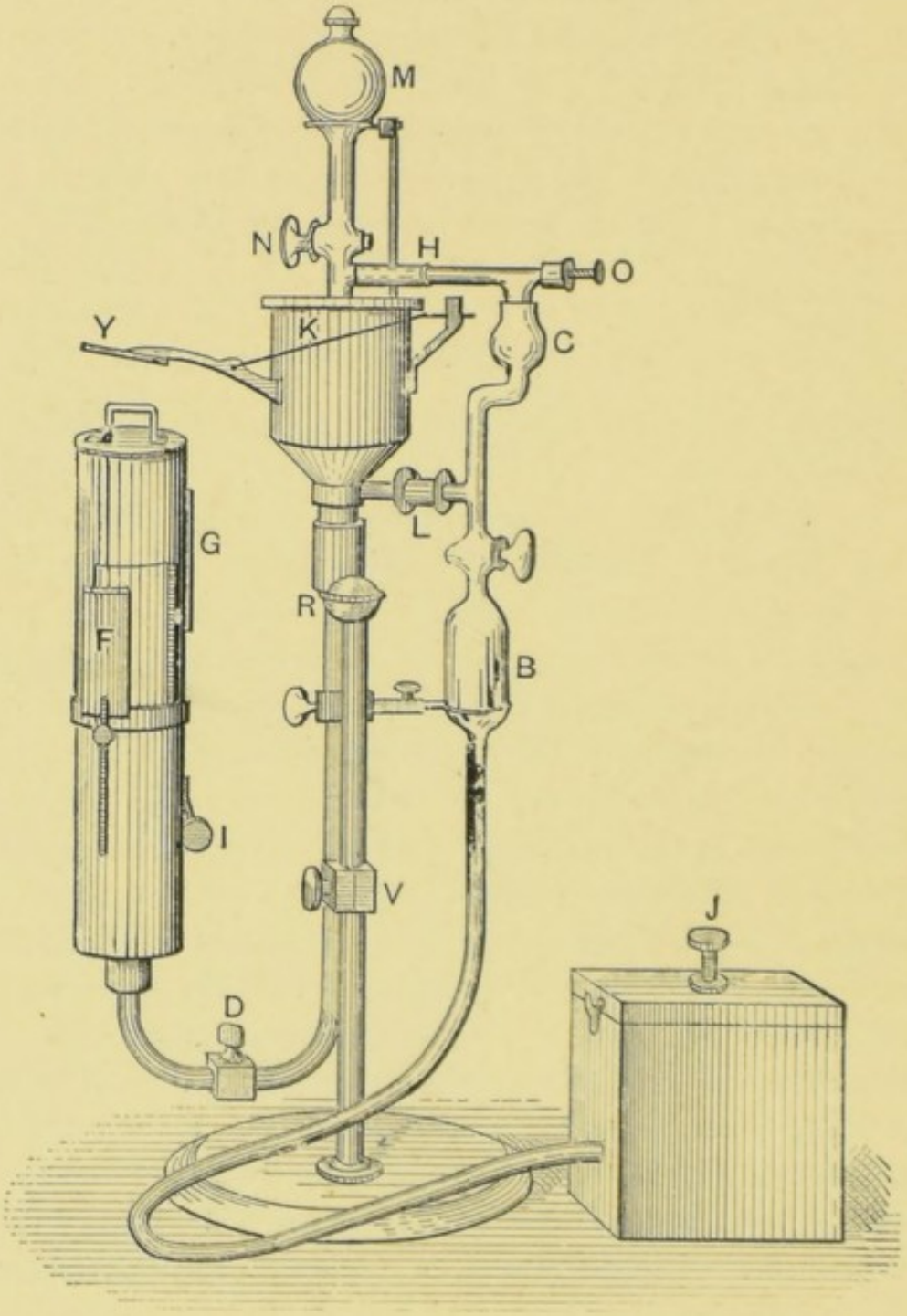


FIG. 3.—Pentane Lamp (Laboratory Model).

candle, which, with a flame 44·5 mm. high, should burn 7·77 grams spermaceti per hour. This, however, is very inconstant, the deviations sometimes amounting to 20 per cent. It has

been used in one important photo-chemical inquiry.[1] In general use at present are the **Vernon Harcourt Pentane Lamp**, and the smaller Simmance modification of this. The former burns a mixture of gaseous pentane and air so as to give at ordinary barometric pressure a flame 2·5 cms. high. Its light is then equal to that of ten Parliamentary candles[2] (see Fig. 3).

The 10 c.p. Pentane-Harcourt lamp (*Journ. of Gas Lighting*, p. 1252 (1898)) is used as standard in London.

Pentane is obtained from American petroleum, B.P. about 40°, and S.G. between 0·6235 and 0·626. Air passes over liquid pentane, is saturated, and burns in a soapstone burner. The flame is restricted above by a chimney, and below there is a conical screen with an opening, through which the lower part of the flame radiates.

The Hefner-Alteneck Amyl-acetate Lamp.—This burns pure amyl-acetate. The wick is circular, the wick-tube being a double cylinder of 8·3 mm. external and 8·0 mm. internal diameter, 25 mm. in length; the whole of the interspace is filled by the lamp, which gives a flame 40 mm. high from the edge of the tube some ten minutes after lighting. With all liquid-fed lamps the intensity rises on first lighting till a more or less constant maximum is reached.

H. W. Vogel gives the following instructions for its use.[3] The height of the flame is determined by the sight line over the two edges of the strip *ab* (see Fig. 4). To adjust, look through the point of the flame at the illuminated edge *ab* and regulate its height by screwing the disc at the side, so that the apex of the bright kernel of the flame just touches the under edge of *ab*. This point of the flame lies about half a millimetre below the furthest point of the external half-luminous mantle.

[1] F. Hurter and V. C. Driffield, Photochemical Investigations, *Jour. of Soc. Chem. Ind.*, **9**, 455 (1890).

[2] For completer details see F. Clowes, *Jour. of Soc. Chem. Ind.*, 313 (1902); Dibdin, *Jahrb. f. Chem. Techn.*, 26 (1888).

[3] For complete description, method of use and determinations according to the Reichsanstalt at Charlottenburg, see *Zeitschr. f. Instr.-Kunde*, **13**, 257 (1893).

The wick should be of coarse fabric, capable of filling the

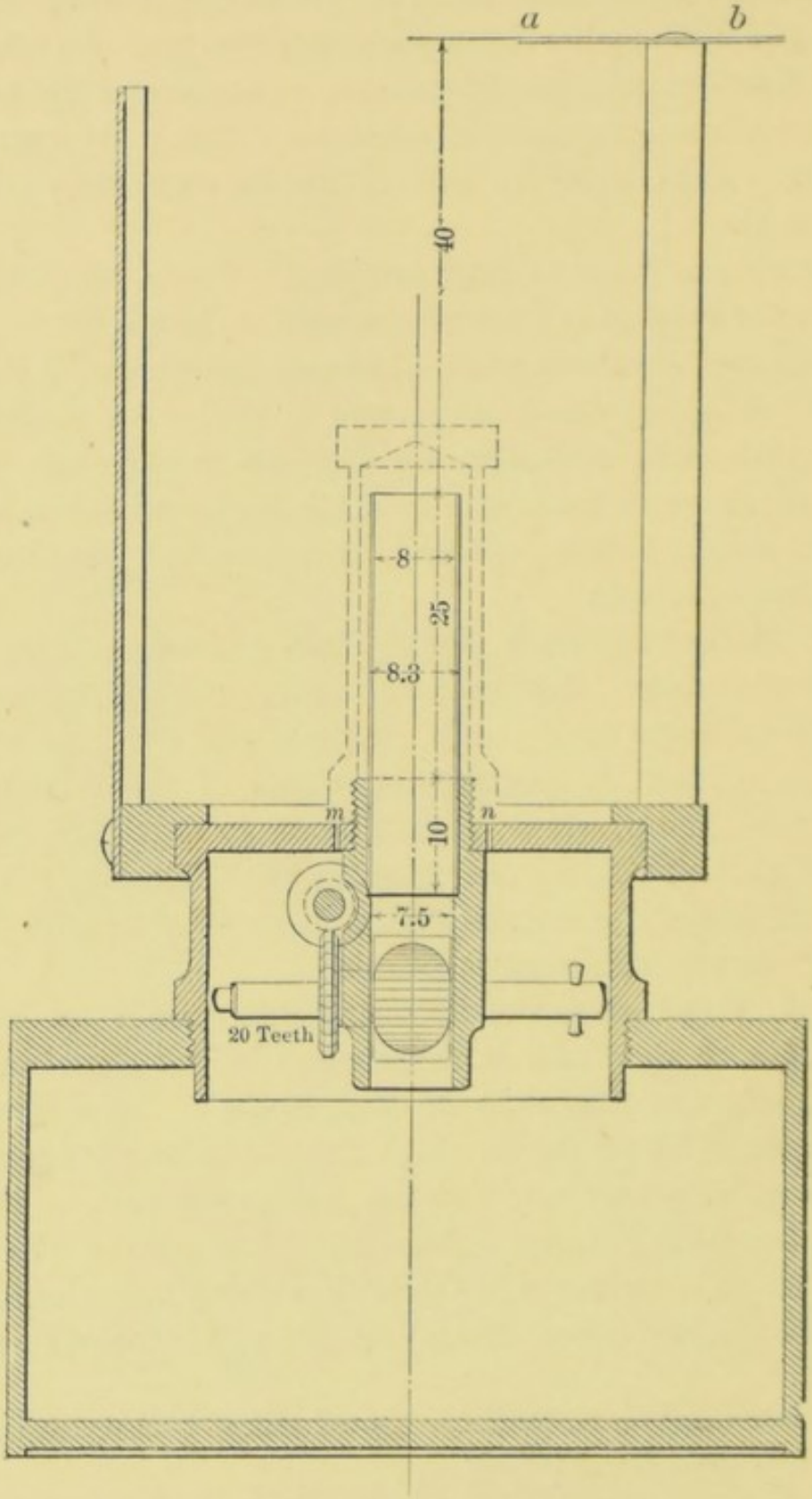


FIG. 4.—Hefner Lamp.

whole cylindrical space, and of absorbing to excess the amyl-acetate, and hence should not be compressed too tightly

in the tube. Mistakes will be at once recognized by a variation of the flame-height. The wick should be so trimmed that the edges of all the threads lie in a plane with the mouth of the tube. So long as the wick can dip into it, the quantity of liquid is immaterial. The intensity of the flame is very sensitive to small variations in its height. As the lamp burns a free flame, without any cylinder or screen, experiments should be carried on in a room free from draughts and vibrations.[1] The influence of impurities in the air is very marked.[2] Liebenthal found that variations in the barometric height produced variations up to 8 per cent. He gives the following formula for his results :—

$$I = 1{\cdot}049(1 - 0{\cdot}0053x)(1 - 0{\cdot}00072x_1) + 0{\cdot}00011(b - 760)$$

where I = light-intensity, x = the vapour-pressure of water, x_1 = the partial pressure of CO_2 (negligible in well-ventilated rooms), and b = barometric height.

The Hefner lamp has not become a universal standard for industrial purposes. The French still prefer the Carcel lamp, burning colza oil ; while in England both the pentane lamp and the candle are used. Of other standards proposed, the platinum unit and the acetylene flame deserve mention. Violle[3] proposed as the unit of intensity the light emitted by 1 sq. cm. of melted platinum on the point of solidification. It involves the use of a constant mixture of oxygen and hydrogen and a special crucible, and has not found much favour. Violle's unit was found by Lummer[4] to equal 26 Hefner units. Siemens has proposed electric heating of the platinum. Violle has also proposed the use of acetylene,[5] streaming from a small conical opening into a wider tube where it mixed with air and burnt in a flat "swallow-tail burner." The use of acetylene as a secondary standard will be dealt with later.

[1] For the use of a silver lamp, see C. H. Bothamly, *Phot. Jour.*, 231 (1894).

[2] Petavel, Eder's *Jahrb. f. Phot.*, 582 (1901) ; Liebenthal, *Zeitschr. f. Instr.-kunde*, **15**, 157 (1895).

[3] J. Violle, *Ann. Chim. et. Phys.*, [6], **3**, 373 (1884).

[4] O. Lummer, *Zeitschr. f. Instr.-kunde*, **13**, 237 (1893).

[5] J. Violle, *Compt. rend.*, **122**, 79 (1895) ; *Zeitschr. f. Beleuch.-wesen*, 384 (1896).

The construction of an absolute standard of light can only be obtained by an international agreement, and the formation of conventions similar to those obtaining in respect of the ohm and the volt. The most constant sources at present obtainable are probably electrically controlled glow-lamps, and it is upon certain intermediate standards of this type, calibrated from time to time on the Vernon-Harcourt 10 c.p. pentane lamp, that the photometric determinations at the National Physical Laboratory are made.[1] The relation of the English standard to the German is approximately—

$$1 \text{ HK} = 0{\cdot}9 \text{ c.p.}$$

The light-unit 1 HK (Hefner-Kerze or Hefner candle) is taken as the mean of protracted observations on a Hefner lamp at the Physik. Techn. Reichanstalt in Charlottenburg, Berlin, for air free from CO_2 and containing 8·8 litres of water-vapour in 1 cubic metre. The following table sums up the terms and units for photometric magnitudes fixed by the Geneva International Congress.[2]

Magnitude.		Unit.	
Name.	Symbol.	Name.	Symbol.
Light-strength or intensity .	I	Candle Hefner	HK.
Amount of light (light-stream)	$\Phi = I\omega = \frac{IS}{r^2}$	Lumen . . .	Lm.
Illumination.	$E = \frac{\Phi}{S} = \frac{I}{r^2}$	Lux (candle-metre) . .	Lx.
Surface-brightness	$\epsilon = \frac{I}{s}$	Candle on 1 cm².	
Light-flux	$\phi = \Phi T$	Lumen hour.	

[1] See "Investigations on Light Standards and the Present Condition of the High-voltage Glow Lamp," being an account of tests made at the National Physical Laboratory by C. C. Paterson, *Proc. Inst. Electric. Engineers*, **38**, pp. 271–348 (1907); also on "The Proposed International Unit of Candle Power," by C. C. Paterson, *Proc. Phys. Soc. London*, xxi. 264 (1909).

[2] On photometric units, see L. Weber, *Elektrotechn. Zeitschr.*, p. 91 (1897).

Here ω = a solid angle
S = surface in sq. metres, s in sq. cms., both in direction normal to the rays
r = distance in metres
T = time in hours

As matters of usage, it may be noted that the term C.P. for candle-power is generally used in England, C.M. is the illumination given by 1 candle-power at 1 metre, and C.M.S. is this illumination for 1 second. The illumination, in candle metres, is known as the "indicated brightness," a term due to Dr. L. Weber.

§ 15. Photometers and Photometry.

The photometric balance is obtained when two brightnesses are equal. The photometer serves to bring two surfaces separately illuminated into optical contact. One is illuminated by the comparison light, the other by the standard. The intensity of one is diminished by one of the methods described in § 16 until a match is obtained.[1]

It follows that if two light sources produce at the same distance the same apparent brightness (*v. supra*) on two completely similar and equal surfaces equally inclined to the direction of the rays, then their intensities or light-strengths are the same. Further, if their intensities are different, the eye cannot judge what is the difference in brightness of the two surfaces, but only that a difference exists. If we cut down the light strength of the stronger till the *difference in brightness* vanishes, then, supposing x to be the quantity by which the greater intensity I_1 has been reduced,

$$\frac{I_1}{x} = I_2$$

assuming that the colours of the lights are exactly the same.

[1] The best method of determining mean horizontal intensity is by a substitution method, in which first a primary standard and then the light-source in question are balanced against the same fixed intermediate standard. See J. A. Fleming, *Journ. Inst. Electr. Eng.*, xxxii., 144 (1901).

The technical difficulties in photometry arise from the facts that (*a*) light-sources are generally different in colour; (*b*) that the difference affects the perception of contrast differently for different brightnesses of the object-field. Some points in this connection will be noticed subsequently, as data of photo-chemical interest for the chemistry of vision. For their technical bearing, reference must be made to treatises on photometry and physiological optics.

A photometer consists essentially in an object-field, or arrangement of two indicating surfaces (termed the photometer head in many instruments) and a mechanism for reducing the strength or amount of light radiated by one of the sources compared.

§ 16. Methods for altering the Light-Strength in a Measurable Way.

Quantitative regulation of the amount of light is of importance both for photometry and for actinometry. The following are the most useful.

Inverse-Square Law.—Usually the photometer "head" or indicating surface, and the two lights to be compared, are mounted on the same optical bench—an accurately divided rigid bar—so that all can be moved in the same line. If one light is kept at a constant distance, and the other moved till the photometric balance is obtained, *i.e.* the brightness of the comparison surfaces are the same, then if i_1 and i_2 be the respective intensities, r_1 and r_2 the corresponding distances—

$$\frac{i_1}{i_2} = \frac{r_2^2}{r_1^2}$$

it being understood that the directions of the rays are the same in both cases. Where light-sources of different sizes are in question and it is desired to compare the specific intensities, this may be accomplished by interposing a diaphragm.

Diaphragms.—This method is familiar to photographers as "stopping down." Only the effect on parallel rays is

considered here. For these, the amount of light is proportional to the size of the aperture. Let I be the strength of a light-source at a distance r from the diaphragm; the illumination upon this is $\frac{Is}{r^2}$, where s is the area of the aperture. The aperture itself functions as a source of light, and at a distance d from the diaphragm the illumination will be—

$$e = \frac{aIs}{r^2 . d^2}$$

where a is a proportionality factor, dependent on the absorption of the medium. This method has often been used in photochemical inquiries in order to obtain a series of graded amounts of light. R. Luther [1] made use of a tube photometer, in which even illumination passed through a series of tubes, the ends of which were covered by apertures of varying size. A sensitometer constructed by Spurge [2] for photographic purposes had circular holes, increasing in a known ratio.

Sector-Wheels and Talbot's Law.—A special case of the use of moving diaphragms is that a rotating disc, out of which a sector is cut through which the light passes. Suppose the angle be a, and I be the original light-strength; then by interposition of the sector it becomes $\frac{I . a}{360}$. Where it is desired to expose a light-sensitive material to a series of increasing amounts of light in one operation, then the sector aperture is cut out in steps. Thus in Fig. 5, which shows the disc of the Hurter and Driffield sensitometer, the angle at the centre is 180°, and each successive angle is one-half the preceding.

In optical photometry it is desirable to have the power of altering the angle while the disc is turning. In its simplest form the instrument consists of two discs with symmetrical sectors of 90°, capable of being closed down. Methods by which this can be accomplished whilst running have

[1] *Zeitsch. physik. Chem.*, **30**, 628 (1899).

[2] *Phot. Jour.*, p. 44 (1881); *ibid.*, 159 (1885). Cf. also Schloemann, *Zeit. wiss. Phot.* (1906).

been devised by Abney[1] and Lummer and Brodhun[2] (see Fig. 6).

The method has the great advantage of simplicity and of not altering the quality of the light. But another factor, viz. *time*, is introduced. It is necessary to assume that intermittent lighting integrates its effect by simple summation. We shall see later that for the photo-chemical effect this is not always the case. For photometry, depending upon the impression on the retina, the method depends on the validity of Talbot's law,[3] which is thus expressed by Von Helmholz:[4]—"If the retina is stimulated by periodically regularly recurring illumination, and if the period of interruption is small enough, then

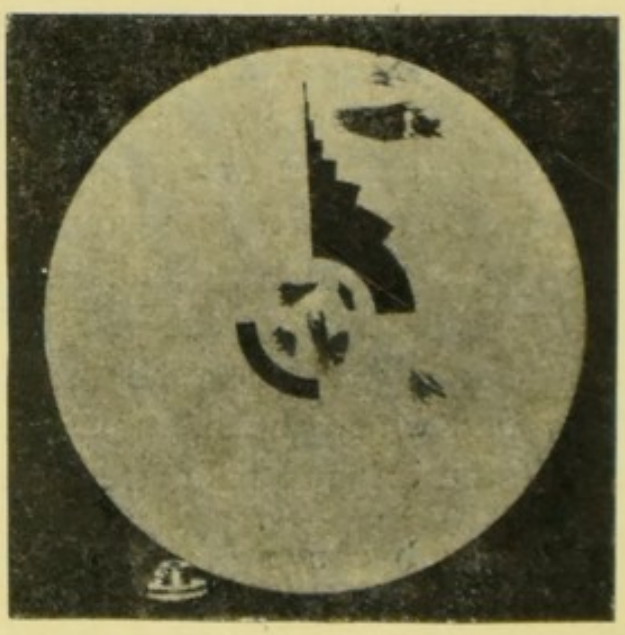


FIG. 5.—Figure of Hurter and Driffield's Wheel.

there is a continuous sensation produced equal to that which would occur if the light incident were continuous over the whole time of illumination." This law has been disputed, but the latest measurements are in its favour.[5] The number of

[1] W. de W. Abney, *Colour Measurement and Mixture* (Swan, Sonnenschein & Co., London).

[2] E. Lummer and O. Brodhun, *Zeitschr. f. Inst. Kunde*, **16**, 299 (1896).

[3] W. Fox Talbot, *Phil. Mag.*, [3] **5**, 321 (1834).

[4] *Physiol. Optik*, 2nd ed., p. 483.

[5] Cf. Plateau, *Physiologie d. Netzhaut*, pp. 30, 34, and 283; Fick, *Pogg. Ann.*, **35**, 457 (1835); Helmholz, *loc. cit.*, *sup.*; Kleiner, *Pflüger's Archiv.*, **18**, 542 (1878); E. Wiedemann, *Wied. Ann.*, **34**, 465 (1888); Lummer and Brodhun, *loc. cit.*, *sup.*

intermittencies for securing a continuous effect is about 40 per sec. for a bright light, decreasing with diminishing intensity.

The Use of Dispersion.[1]—In order to diminish intensity,

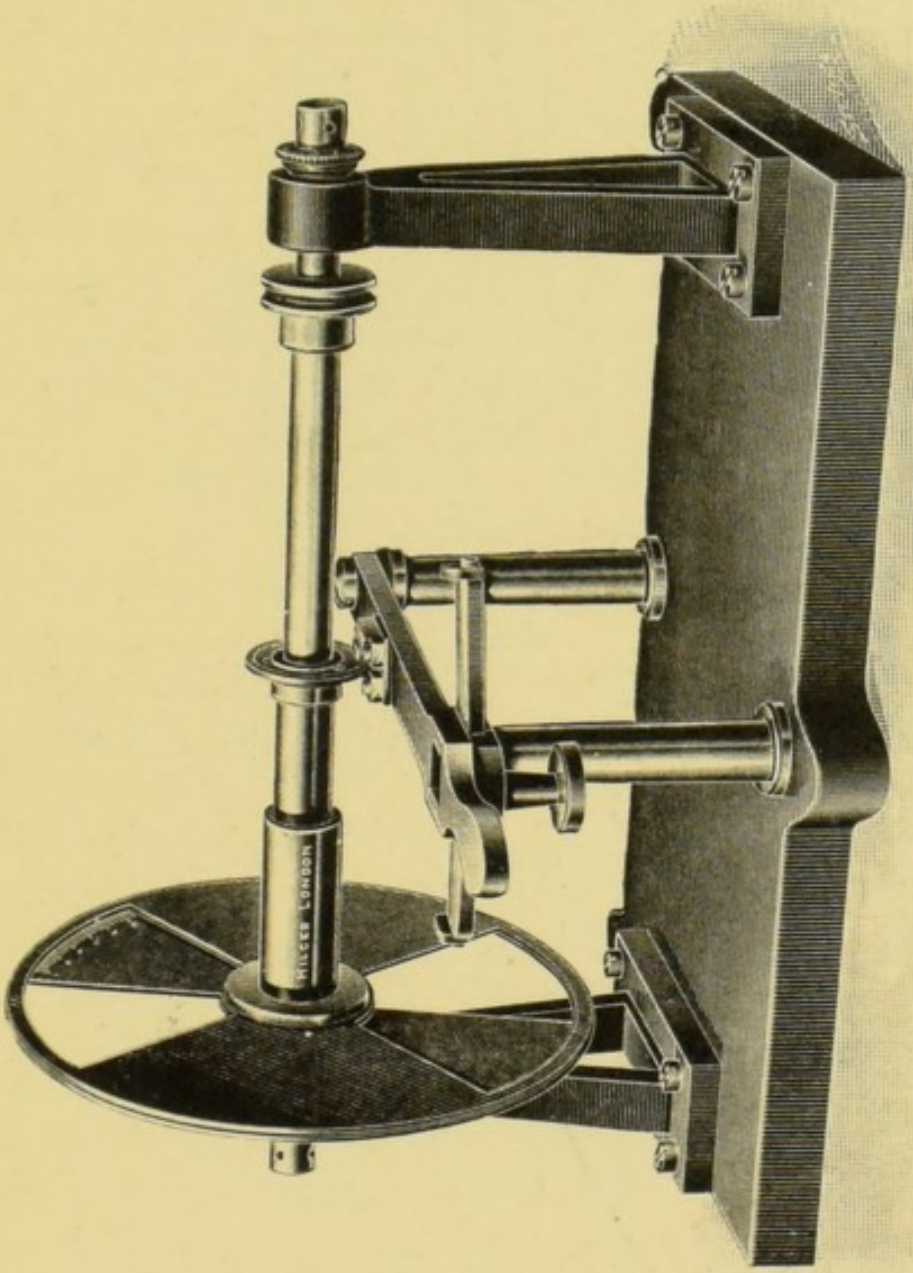


FIG. 6.—Abney Sector (Colour-measurement).

advantage may be taken of the properties of diverging lens-systems. Consider a double concave lens at a distance p

[1] The method has been worked out practically by H. Krüss for the photometry of intense light-sources (a dioptric light-diffuser). Eder's *Jahrbuch f. Phot.*, p. 90 (1906).

from a light-source, and a screen or illuminated surface at a distance d, so that the distance of the screen is $p + d$.

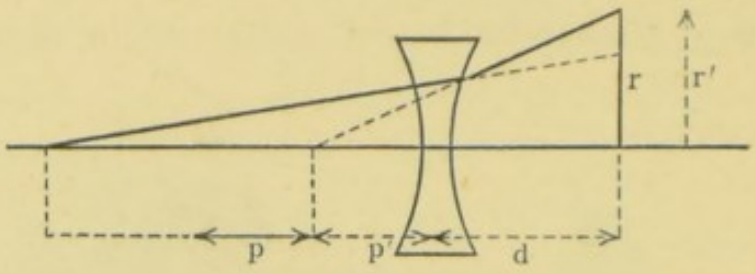


FIG. 7.

Then the rays seem to come from the source at the distance p', the refracted pencil illuminating a circle of radius r' instead of r, whence the intensities are as $r^2 : r'^2$. If f be the focal distance, we have the usual relation—

$$\frac{1}{p'} - \frac{1}{p} = \frac{1}{f}$$

$$p' = \frac{pf}{p + f}$$

If the radius of curvature of the lens be ρ, then—

$$\frac{r'}{\rho} = \frac{p' + d}{p'} \quad \text{and} \quad \frac{r}{\rho} = \frac{p + d}{p}$$

hence

$$\frac{r'}{r} = \frac{p(p' + d)}{p'(p + d)} = 1 + \frac{pd}{f(p + d)}$$

so that the intensities are as—

$$\left(\frac{r'}{r}\right)^2 = \left[1 + \frac{pd}{f(p + d)}\right]$$

The value of this method is lessened, especially for photo-chemical work, owing to absorption of light in the glass, as well as by the reflection from its surface. In the formulæ above, these conditions are not expressed.

Polarization.—The properties of plane polarized light are utilized in several ways in photometry, especially in spectro-photometry, and these methods will be described in connection with certain instruments.

§ 16A. PHOTOMETERS AND STANDARD LIGHT SOURCES.

We may conveniently classify these as instruments for comparing total light effects, and instruments in which the light is decomposed, and the measurements made for narrow spectral regions.

The former differ principally in the arrangement for the indicating surface, or the "Photometer head." In the Rumford photometer, a rod placed before a white screen is illuminated by the two light-sources, when two shadows are formed. These appear equally bright when equally illuminated; the intensity of the comparison light is altered till a match is reached. Abney[1] has modified this method by using a special screen, which enables the two light sources to be fixed, and the juxtaposed shadow-images made equally bright by moving the rod. Mr. Chapman Jones[2] has designed an opacity meter and an opacity balance based on the Abney screen.

The Bunsen "Grease-spot" Photometer.—A piece of good homogeneous paper is uniformly warmed on a plate. In the centre of this a small circlet or annulus is described with a little melted stearin on a fine brush. This ring is allowed to cool; there is a free unwaxed spot within the boundary thus made, which must now be filled with melted wax, well pressed into the paper. The previously formed boundary secures a well-defined spot. Viewed in incident light, the grease spot appears darker than the surrounding paper; by transmitted, lighter; on equal illumination, the distinction vanishes. Krüss[3] uses two reflection prisms, which reflect the two sides of the spot and bring them at right angles to the line of vision. The eye sees two fields separated by a fine line, which disappears when they are brought to equal brightness.

The Lummer-Brodhun Photometer.—A defect of the Bunsen photometer is that the grease spot not only transmits light, but reflects it, while conversely under the same illumina-

[1] W. de W. Abney, *Instruction in Photography*, 10 edit., p. 134.
[2] C. Jones, *Phot. Journ.*, p. 86 (1895); *ibid.*, p. 99 (1898).
[3] Eder's *Jahrb. f. Phot.*, p. 321 (1901).

tion, the surrounding paper transmits as well as reflects. This greatly lowers the possible sensitiveness,[1] which would reach its maximum if the external field transmitted no light but reflected all. A very close approximation to this optimum was made by Swan.[2] Two equal right-angled prisms are pressed together upon a small patch of Canada balsam till a circular patch is formed. Light falling on this is transmitted; that falling outside is totally reflected, as is diagrammatically shown on Fig. 8.

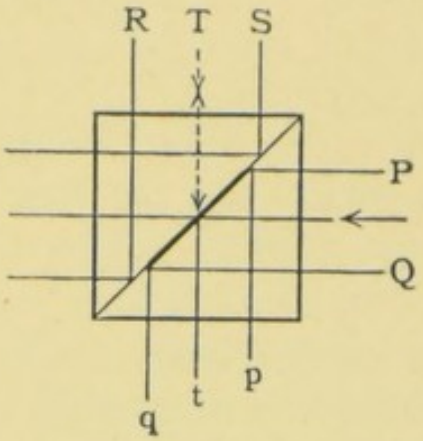


FIG. 8.

The eye at q, t, p, sees the ray-bundle t from RTS, RS being reflected, and p, q from P, Q, the centre portion being transmitted. When both are equally illuminated, the distinction vanishes. The principle was rediscovered by Lummer and Brodhun,[3] who have introduced many improvements.

S is a screen of optically worked gypsum; the light from

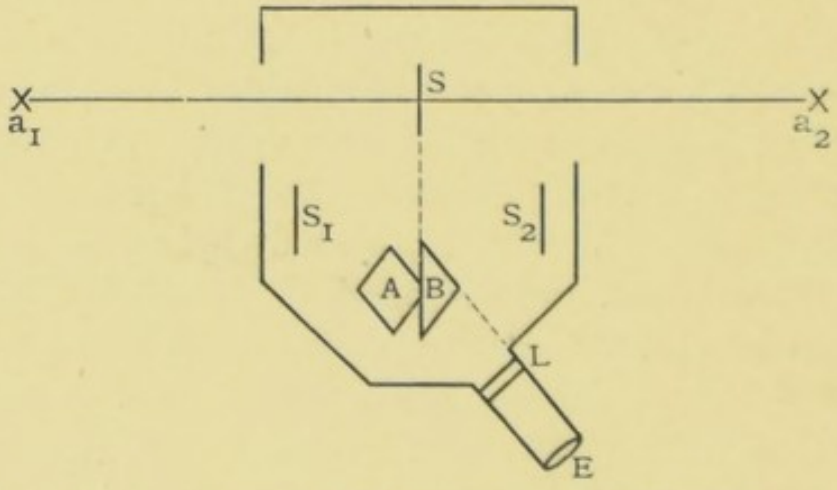


FIG. 9.—Lummer and Brodhun's Photometer.

the two sources a_1 and a_2 is reflected by mirrors at $s_1 s_2$, and thence to the optical cube; this consists of two right-angled

[1] Cf. L. Weber, *Wied. Ann.*, **31**, 676 (1887).

[2] J. W. Swan, *Trans. Roy. Soc.*, Edin. XXI.

[3] O. Lummer and E. Brodhun, *Zeitschr. f. Inst. Kunde*, **9**, 44 and 61 (1889).

prisms A and B; part of the spherical face of A is cut off and the surfaces pressed against the hypotenuse of B so that there is no film of air between, the use of optically worked flats dispensing with the Canada balsam. The observer's eye at E focusses the indicating surfaces by means of an ocular perpendicular to the base of B. Krüss' double-prism arrangement may also be used, as with the Bunsen head. Marten's photometer[1] makes use of a bi-prism to bring the illuminated surfaces into optical contact. Joly's diffusion-photometer[2] consists of two right-angled prisms of a translucent substance (paraffin, ground glass) which are placed with a thin strip of silver foil separating the two longer sides; when the hypotenuses are equally illuminated, the bases appear to an observer's eye of equal brightness. Wild[3] constructed a photometer for polarized light which depends on the vanishing of interference fringes caused by the incidence of an extraordinary and an ordinary ray of different intensities falling on a Savart double plate.[4] Obviously, it can only be used for unpolarized or depolarized light.

Weber's Universal Photometer.—These photometers must be used in a dark room. A completely enclosed photometer, by which a variety of light measurements may be made, has been designed by Dr. L. Weber.[5]

The accompanying diagram shows the arrangement. A comparison light-source *s* is contained at one end of the fixed internally blackened tube A, and illuminates a vertical milk-glass plate S, which can be moved along the tube, its position being indicated by a scale marked outside. A second tube B is capable of free rotation round the axis of A, and contains at its junction with A the Lummer-Brodhun cube P and a diaphragm *d*. It is provided with a further extension R, to prevent side light entering, the light to be measured

[1] F. F. Martens, *Verh. deutsch. Phys. Ges.*, **1**, 278 (1899).

[2] J. Joly, *Phil. Mag.*, [5] **26**, 26 (1888).

[3] O. Wild, *Pogg. Ann.*, **99**, 235 (1856).

[4] See *e.g.* T. Preston, *Theory of Light*, 2nd edit., p. 404.

[5] *Zeitschr. f. Elektrotechnik*, Hft. 7, 8 and 9 (1889); *Wied. Ann.*, **20**, 326 (1883).

illuminating a fixed milk-glass plate *m*. Then the eye at *e* sees the middle field lit from *m*, the outer from S.

Weber found that the intensity of the benzine lamp[1] used as the comparison-light *s*, is a linear function of the height of flame; $i = a + bh$, where *a* and *b* are constants. A standard

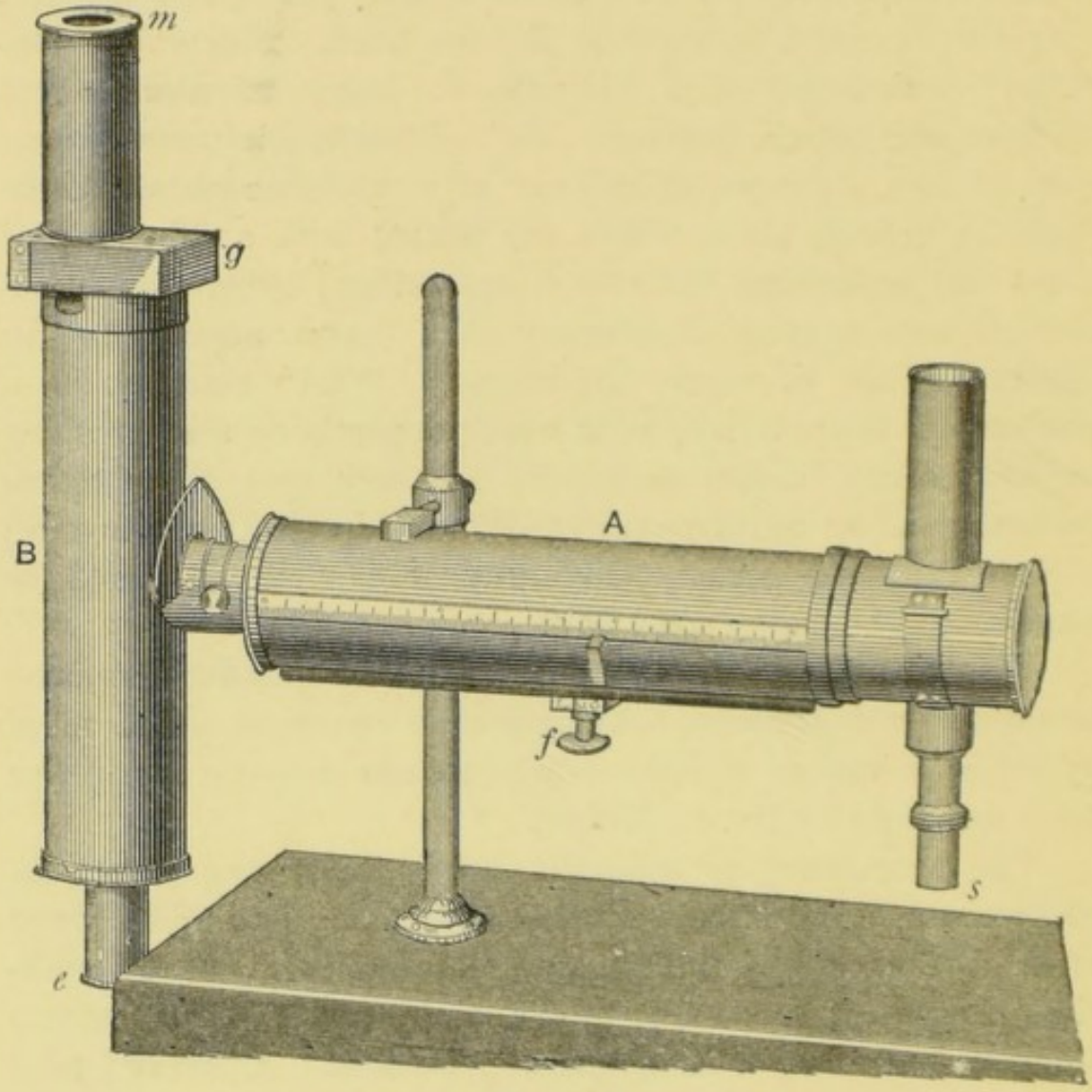


FIG. 10.—Weber Photometer.

height of 20 mm. is usually taken, and from this relation, a correction can be applied for any variation in the height. From 19 to 21 mm. a variation of 0·1 mm. corresponds to 1 per cent. variation in the measured result. In comparing two light sources, each is allowed to illuminate the milk-glass plate at *m* in turn, and the milk-glass plate at S is moved till a balance is obtained. To reduce an inconvenient intensity,

[1] See later under "Light Sources for Special Purposes."

other milk-glass plates can be inserted at *m*, the weakening coefficients being obtained by previous calibration in the photometer. Instead of these, two Nicol prisms may be used, the use of which will be described later.[1]

When it is desired to measure the intensity of a light-source, the indicated brightness of an illuminated surface, or

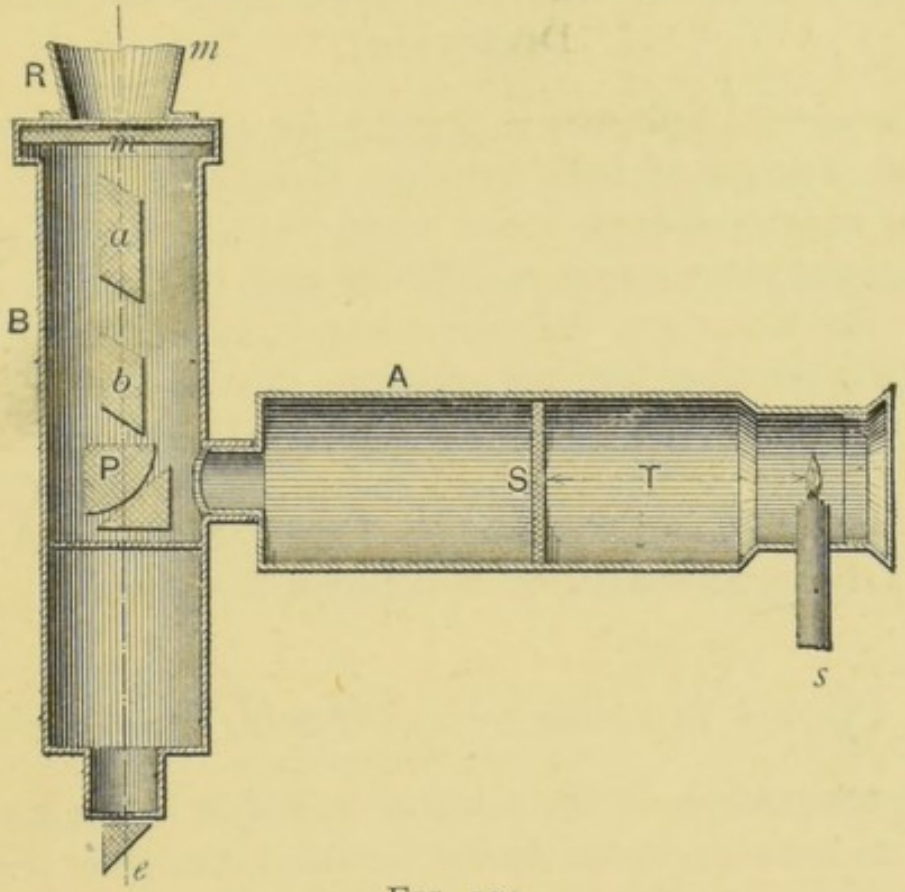


FIG. 10A.

the amount of diffuse light (such as daylight) in any given direction, the movable tube of the photometer is pointed with its axis in the given direction, and a measurement made by comparison with the enclosed benzine flame. The measurement may then be reduced to standard terms by comparison of the intensity of the normal benzine flame with that of a standard source of light.[2]

[1] L. Weber, *Schriften d. naturwiss. Ver f. Schleswig-Holstein*, **8**, H. 2 (1891).

[2] For further details see Weber, *loc. cit.*; H. W. Vogel, *Hdbuch. d. Photo.*, ii., p. 12, 4th edit. Benzine is a particular fraction of light petroleum, as to the characterization of which *cf.* J. M. Eder, *Beiträge zur Photochemie*. W. Knapp. An electric glow-lamp, with potentiometer control, may be substituted with advantage.

For other universal photometers, and for photometers for determining the light-flux (for definition of which see table on p. 24), reference must be made to works on the subject, as Palaz or Brodhun.[1]

§ 17. Photometry of the Light Strength in Different Directions.

A theoretical light-source, a point, for example, sends forth the same amount of light in every direction. But ordinary artificial sources diverge more or less widely; there may be differences of temperature in different parts of the source, and shadow formation may be more or less inevitable. This is particularly the case with the arc lamp, the intensity of which varies rapidly as the horizontal direction is departed from. In addition to ordinary measurements, made for different directions, integrating photometers have been designed which permit a direct determination of the total light-flux.[2]

§ 18. Colour Photometry and Flicker-Photometers.

The comparison of light-sources described in the foregoing paragraph is based on the assumption that they differ but little in colour. The perception of contrast is markedly lessened as the difference in colour increases. Moreover, even if the surface-brightnesses be equal for one absolute intensity, they will not appear so for others. This is known as Purkinjé's phenomenon, which may be thus indicated:—If a red and a blue field be of equal brightness, and then the illumination of both be decreased in the same proportion, the blue appears brighter than the

[1] A. Palaz, *Photometry; a Treatise for Industrial Purposes*, trans. by Patterson (Sampson, Low, Marston & Co.); O. Brodhun, *Art. Photometry* in Winkelmann's *Hdbuch. d. Physik.*, 2nd edit. ii., p. 770 (J. A. Barth, Leipzig, 1906).

[2] A. Blondel, *C.R.*, **120**, 311, 550 (1895); R. Albricht, *Elektrot. Zeit.*, **21**, 595; **26**, 312 (1900). For calculations with electric lamps, see P. Högner, *Elektrotechnik in einz. Darst.*, viii. (Vieweg, Brunswick); and K. Schaum, *Photochem. u Photogr.*, Bd. i. p. 125 (Barth, Leipzig).

red. This is further a function of the size of the surface, for on diminishing the surface areas of both of the now unequally bright fields, a limit is reached, when both appear again equally bright.[1]

Usually, in comparing two light sources of considerably different colour, the difference is removed or lessened by cutting out the same spectral region by coloured glasses and measuring for this. But obviously it is not legitimate to deduce the ratio of the total intensities by this method. M. de Lépinay [2] uses two light-filters, one transmitting red, the other green, and compares the lights for both. If R is the ratio for red, G for green, and N for the total intensities, according to Lépinay $\frac{R}{N} = 1 + 0{\cdot}208\left(1 - \frac{G}{R}\right)$. A similar method is used by Weber in his photometer,[3] but this is only a slightly better approximation, in view of the great variation of the spectral emission curves of different light-sources. Siemens and Weber have proposed methods depending on visual acuteness, but the results are not satisfactory.

Flicker Photometers.—It is claimed for flicker photometers that the measurements are independent of the Purkinjé phenomenon. Talbot's law is valid not only for rapidly consecutive illuminations of different intensity, but also when these are qualitatively different. If a surface is alternately lit by lights of different colour and intensity, a mixed colour is seen when the rate of alternation is sufficient, otherwise the sensation known as "flicker" is produced. Now this limit is attained for a smaller number of periods according as the difference of intensities is less. Hence, by adjusting the intensities till the

[1] This dependence on the area is due to the fact that for the *fovea centralis* and the *macula lutea*—the rodless region of the retina—the Purkinjé phenomenon is absent (J. von Kries in W. Nagel's *Hdbuch. d. Physiologie*, p. 182 (1904)). K. Schaum (*Zeit. f. Wiss. Phot.*, iii. 272 (1905)) suggests that the curve of spectral brightness for a mean intensity is produced by summation of curves for a very high and very low intensity, corresponding to the curves for the rods and cones separately.

[2] C. R., **97**, 1428 (1883).

[3] *Zeitschr. f. Elektrotechnik*, *loc. cit.* (1889).

"flicker" for a certain rapidity just vanishes, the relative intensities alone may be measured. Photometers on this principle were first constructed by Rood.[1] In one form, a strip of finely ground glass is alternately illuminated. Krüss [2] used a movable screen, consisting of two discs, with a portion of their peripheries removed, and rotating in opposite directions; and later,[3] a cylinder oscillating through an angle of 90°. If this be the angle between the axes of the beams of two light-sources as they converge at the axis of the cylinder, the semi-surface of the cylinder is fully illuminated by each light in turn; the eye regards the mean field between the two extreme portions, and the "flicker" vanishes for equal illumination. Simmance and Abady's photometer [4] consists of disc-shaped surface of white substance (gypsum or better compressed magnesia), the circumference being bevelled in a particular manner. This is rotated by a motor at a regular speed before the observing ocular. At right angles to the line of sight and in line with the axis of the disc are the two lights to be compared. Their rays fall on the bevelled periphery, which is so cut that alternately illuminated surfaces present themselves to view. Other devices have been designed by Bechstein [5] and Krüss.[6] The latter authority on photometry points out that so far, it has only been shown that different observers get corresponding values for differently coloured light sources, and not that the values obtained are identical with the physiological brightness. It may be noted here that the persistence of light-impression is different for different colours,[7] which may be due to the physico-chemical processes corresponding to the act of vision having a different velocity for different colours. For accurate comparison of hetero-

[1] O. N. Rood, *Amer. Journ.*, [3] **46**, 173 (1893); *ibid.*, [4] **8**, 194 (1899).

[2] H. Krüss, *Phys. Zeitschr*, **5**, 65 (1904).

[3] See also F. P. Wittman, *Phys. Rev.*, **3**, 241 (1896).

[4] *Proc. Lond. Phys. Soc.*, **19**, 39 (1904); *Phil. Mag.* (1904).

[5] W. Bechstein, *Zeitschr. f. Instr. Kunde*, **25**, 45 (1905).

[6] H. Krüss, *Zeitschr. f. Inst. Kunde*, **24**, 256 (1904); *ibid.*, **25**, 98 (1905).

[7] Cf. F. Allen, *Phys. Rev.*, **11**, 257 (1900).

chromic light-sources, as well as for many other measurements of light, it is necessary to resolve the light spectrally, and make use of the methods and instruments of spectrophotometry.

§ 19. Spectrophotometry.

The method employed in spectrophotometry consists in the juxtaposition of two spectra, one of which is that to be measured, the other the standard for comparison. An arrangement at the ocular permits a narrow strip in any desired region of a continuous spectrum to be screened off by a diaphragm, so that the contrast in question can be measured throughout the spectrum. Beyond the visible spectrum there can be substituted for the eye, in the infra-red region a bolometer or linear thermopile or radio-micrometer placed in the ocular slit; or in the ultra-violet region a photographic plate.

Govi [1] and Crova appears to have been the first to use two contiguous spectra for comparative measurements. For absorption work, the method was developed by K. Vierordt [2] who based a system of quantitative analysis on it. He used a double slit, each half being controlled by a separate screw. Owing to the fan-like extension of the spectrum, the brightness of any part of the spectrum is approximately proportional to the width of the slit. Error is introduced in that when one slit is wider than the other, the spectra are then of different purity and the ocular slit is not subtending the same spectral region in each. This failure was recognized by Vierordt himself; and he used smoked glasses to cut down the intensity, and then made a final adjustment with the slit. Krüss [3] introduced a double symmetrical slit, in which both slits remained adjusted about the same middle line, and to ensure

[1] *Compt. rend.*, **50**, 156 (1860).

[2] *Pogg. Ann.*, **140**, 172 (1870); and *Die Anwendung des Spectral apparates zur Photometrie der Absorption-spectra.* (Tübingen, 1873.)

[3] See G. and H. Krüss, *Quantitative Spektralanalyse*, p. 89. (Hamburg, 1891.)

the better contiguity of the images, added the Hüfner-Albrecht rhomb.

§ 20. Polarization Spectrophotometers.

In these the diminution of the intensity is brought about by some polarizing adjustment in certain instruments, adjustment is made to equal visual brightness, and in others this is judged by the disappearance of interference fringes. The latter method is theoretically the more sensitive, but as Kayser remarks, involves more strain on the observer and hence fails in the promised increase of accuracy. Of the first class we have—

Glan's Photometer.[1]—In this the collimator slit is divided into an upper and lower half by a metal strip some 2 mm. broad. Adjustable racking of the collimator makes this form a fine dividing line between the two spectra, but the adjustment is different for each region. Gouy[2] makes the strip wedge-shaped and slides it along till the right width intervenes. The light from the slit, after traversing the collimator objective, meets a Wollaston prism, the principal section of which is parallel to the slit, so that of each slit image an ordinary and an extraordinary ray are formed. The collimator adjustment is made so that the upper edge of the image of the metal strip in the extraordinary ray exactly coincides with the lower edge of the same image in the ordinary ray. Hence, meeting at the bounding line we have two spectra, their vibrations being polarized at right angles to each other. The alteration of intensity is effected by a Nicol prism, adjustable with a divided circle. If the Nicol is rotated from its zero point through the angle α, then the ratio of the intensities is given by $I = I_0 \tan^2 \alpha$. It is necessary, however, to make a series of special adjustments to obtain the actual transparency of any substance.

[1] P. Glan, *Wied. Ann.*, **1**, 351 (1887); **3**, 54 (1878).
[2] *Ann. de Chim. et Phys.*, [5] **18**, 5 (1879).

Hüfner's Spectrophotometer.[1]—This differs from Glan's in that only one of the bundles of rays is polarized. I shall describe here briefly the improved form, made by Hilger,[2] which differs only in its spectral adjustments from Hüfner's second model. For absorption measurements the Welsbach burner, A, gives a convenient light,[3] a slightly diverging cone of rays being used, and the light from this passes through Hüfner-Albrecht rhomb, B, before it reaches the slit of the spectroscope. This is a prism of two plane-parallel surfaces, and divides the rays into two bundles separated by a vanishingly fine line. Before the lower half of the rhomb is placed a small polarizing Nicol, C; before the upper half there can be moved by a graduated rackwork adjustment a smoked glass wedge, the absorption by which compensates for that due to the Nicol. At the slit we have two fields in contact, the upper one polarized (the positions of the fields are reversed by the rhomb), but otherwise unchanged, the lower one diminished in intensity by the absorption to be measured. Where the emission-fields of two light sources have to be compared, a head consisting of two metal prisms with surfaces of optically worked gypsum is substituted for the absorption-stand. The vertical surfaces are at right angles to each other, but make an angle of 45° with the optic axis of the photometer. They are then illuminated by the two light sources, placed at right angles to the axis of the photometer, when the relative emission can be compared. If one prism be removed, and another substituted, on which any desired surface is fastened, the reflecting power throughout the spectrum can be compared with that of the gypsum surface.

After passing through the collimator, E (Fig. 11A), and the dispersion prism, F, the rays of both fields enter an analyzing Nicol, which can be rotated on its axis, the rotation being measured with a vernier on a divided circle, H. They then

[1] *Journ. f. prakt. Chem.*, [2] **16**, 290 (1877), and *Zeitschr. f. physik. Chem.*, **3**, 562 (1899).

[2] C. E. K. Mees and S. E. Sheppard, *Phot. Journ.*, **44**, 200 (1904); *Zeit. wiss. Phot.*, **2**, 203 (1904).

[3] An *osmium* filament lamp may be substituted for this.

pass through the telescope, the fields being optically reversed by the eyepiece, so that the field diminished by absorption, or

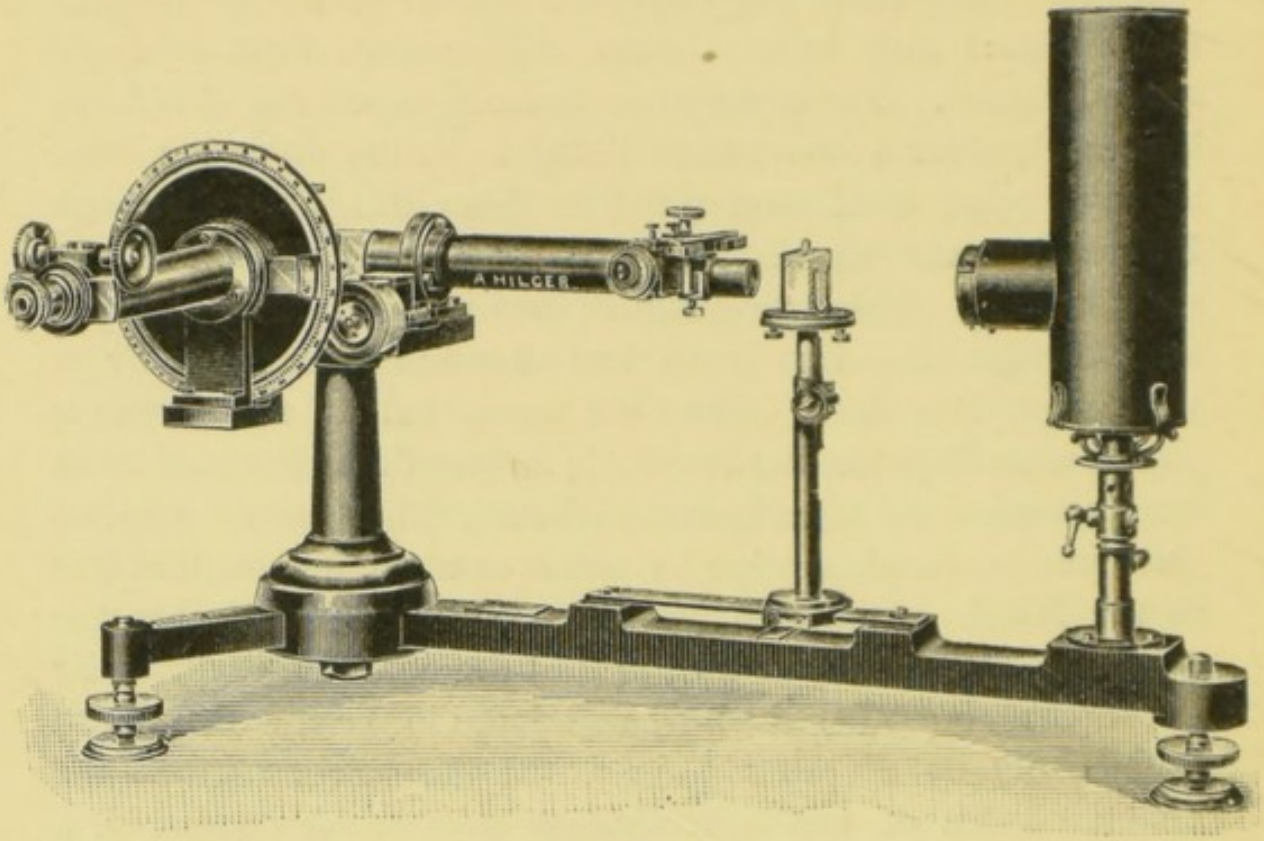


FIG. 11.

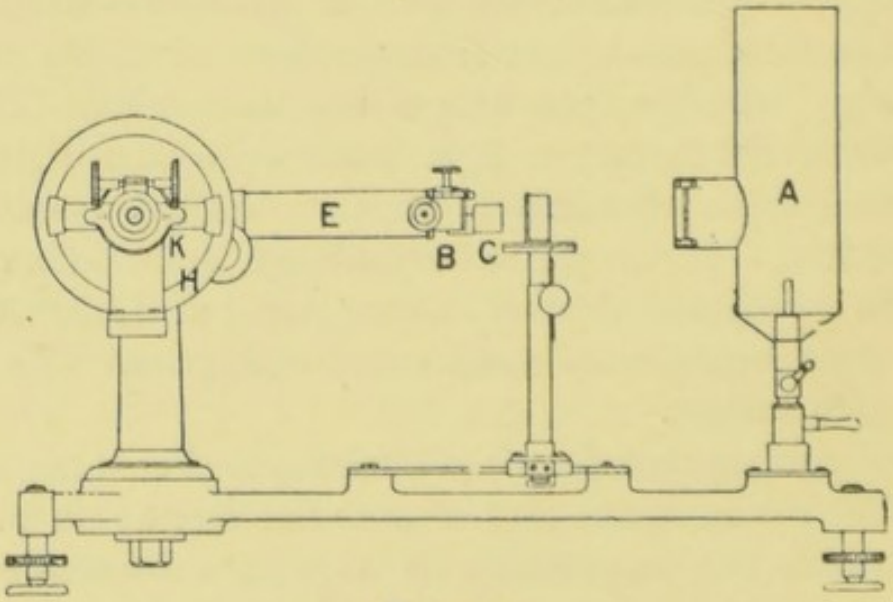


FIG. 11A.

other "object" field,[1] is again uppermost. To make measurements, the Nicols are first set accurately parallel. This is

[1] This appears to be a convenient phrase for such circumlocutions as "the field of the light to be compared," etc.

best achieved by measuring the absorption of a photographic negative.[1] When the analyzer is set at zero, the slight absorption due to the Nicol is adjusted by means of the smoked glass wedge. The light passing through crossed Nicols is proportional to the square of the cosine of the angle between them, hence $I = I_0 \cos^2 \theta$, where θ is the angle on the circle of the analyzer.

In the new model, the prism is of the constant deviation type,[2] the wave-lengths being given direct on the drum of the screw which moves the dispersion-prism table. This has the further advantage that the addition of two 30° prisms converts the prism into a simple total reflection prism, whereby the instrument can be used as a total-photometer for white light. The calibration of the ocular slit, *i.e.* determination of what wave-lengths are comprised in any slit-width, is carried out as follows:—One edge of the ocular slit is fixed at zero, and a given spectral line (middle of D line, *e.g.*) brought into alignment. This edge is then moved through the desired distance on the ocular scale and the spectral line again made to coincide. The corresponding values of the ocular and wave-length scales which should be obtained for different parts of the spectrum, enable a calibration table to be constructed.

Recently F. Twyman ("Improvements in the Hüfner Type of Spectrophotometer," *Phil. Mag.*, April, 1907) has pointed out a universal source of error in all polarizing spectrophotometers, viz. that the light on transmission through the dispersion prism is already polarized, whether it be an ordinary prism of 60° or of the constant deviation type, owing to unequal reflection of vibrations in and at right angles to the plane of polarization. The intensity of the comparison beam may thus vary some 30 per cent. It may be compensated in the Hüfner (and presumably the König) instruments by choosing the glass and angles of the Hüfner rhomb so as to produce

[1] Theoretically, when $\theta = 90°$, the extinction should be complete; practically, the analyzer is set at 90°, and the Nicols adjusted till a maximum extinction is obtained. Then the absorption of a negative is measured on two quadrants, and the front Nicol rotated till the same value is obtained in each.

[2] See E. C. C. Baly, *Spectroscopy*, in this series, pp. 57, 58, 117.

a partial polarization equal to that in a plane perpendicular to its own produced by the dispersion prism.

Where high extinctions have to be measured, a convenient adjunct is a subsidiary extinction, which is best made of a photographic plate developed with ferrous oxalate and used, after careful measurement of its light-absorbing power, as a cap on the polarizing Nicol.

Since $I = I_0 \cos^2 \theta$, the extinction-coefficient (*vide* p. 136) $\epsilon = -2 \log \cos \theta$.

Other polarizing spectrophotometers have been designed by Glazebrook,[1] Crova,[2] A. Wild,[3] A. König,[4] and J. Königsberger.[5] The photometers of Wild and Königsberger utilize the vanishing of interference fringes as a criterion that the two fields are equal. Two ray-bundles proceeding from a divided collimator-slit are polarized by a Senarmont or Thomson prism,[6] and then pass through a rhomb of Iceland spar. There issues from this a single ray-bundle, consisting of the ordinarily refracted ray from one-half of the slit, and the extraordinarily refracted rays from the other. This, after passing the dispersion prism, traverses a Savart[7] interference plate, and, finally, another polarizing prism. Interfering fringes in the Savart plate vanish when the united bundle contains equal quantities of light polarized at right angles to each other, *i.e.* when $I = I_0 . P \tan^2 \alpha$, where α is the angle which the plane of polarization of the first polarizing prism makes with the principal section of the Iceland-spar rhomb, and P is an empirically determined constant. Königsberger's instrument was a microphotometer, based on the same principle, for determining the absorption relations of crystals.[8] As before remarked, the

[1] *Proc. Cambridge Philos. Soc.*, **4**, 304.

[2] *Ann. de Chim. et Phys.*, [5] **29**, 556 (1883).

[3] *Wied. Ann.*, **20**, 452 (1883).

[4] *Ibid.*, **53**, 785 (1894).

[5] *Zeitschr. f. Inst. Kunde*, **21**, 129 (1901); **22**, 129 (1902).

[6] For different forms of polarizing prisms, see T. Preston, *Theory of Light*, 2nd edit., pp. 312–315, 449–466.

[7] See Preston's *Light*, p. 402.

[8] T. Königsberger, "Dependence of Absorption of Solid Bodies on the Temperature," *Ann. d. Phys.*, [4] **309**, 796 (1901).

greater sensitiveness claimed for the method is probably rather apparent than real.

König's spectrophotometer has been recently remodelled by Martens and Grünbaum,[1] and, on account of its use in several important investigations, demands some description. In the spectrophotometers just described the observer looks at the spectrum itself, or, rather, at a very narrow band cut out by a narrow ocular slit. Even with a narrow slit, if the object field (absorption) be changing rapidly with wave-length, the strip is unevenly illuminated. To avoid this König used the Maxwell observing method, in which the ocular is dispensed with, and the eye, brought in the focal plane of the spectrum, looks at the objective. This is then seen illuminated by the light which passes the pupil, or a narrow slit brought before it.

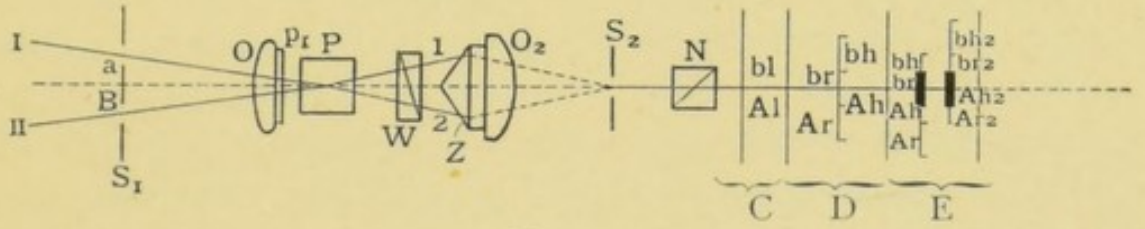


FIG. 12.

The new construction is, in essentials, a spectroscope with the refracting edge horizontal, so that the two fields produced for photometric comparison lie vertically. Fig. 12 gives a schematic plan of the arrangement. The collimator slit s_1 is diaphragmed to give two slits, *a* and B; the two light-bundles fall on the objective op_1, pass the dispersion prism P, the Wollaston prism W, and then the biprism Z, which secures optical contiguity of the two fields, with no sensible dividing line at equal brightness. They next pass through the telescope objective O_2, and form in the plane of the ocular slit s_2 eight spectra, which are shown analyzed at C, D, and E.

If W and Z were not present, there would be, as shown at C, of *a* a spectrum at A, of B one at *b*. By the action of W the case becomes as at D, giving four spectra. Each of these is in turn divided by the biprism Z, giving the case shown at

[1] F. F. Martens, *Verh. deutsch. phys. Ges.*, **1**, 280 (1899); F. F. Martens and F. Grünbaum, *Ann. d. Phys.*, [4] **12**, 894 (1903).

E, four spectra, A*r*, A*h*, *br*, *bh*, from the one half of the prism, four at Ar_2, etc., from the other half. Only the light of the central images *br* and Ah_2 is transmitted through the ocular slit. On the axis there lie, therefore, two exactly contiguous spectra, polarized at right angles to each other, the one from the first slit and the lower[1] prism half, the other from the second slit and the upper prism half. Looking through the ocular, the biprism is illuminated by the homogeneous light transmited by s_2.

The Illuminating Arrangement.—A special feature in the new König instrument is the device for illuminating the two slits of the collimator with parallel rays from the same portion of the light source. A small milk-glass window, by a system of three lenses, throws two real images on the slits *a* and B; the two parallel bundles are brought accurately through the slits on to the corresponding halves of the biprism. This permits of the use of long tubes (up to 30 cms.) for dilute solutions of absorbing substances. In the case of solutions of colouring matters (salts, dyes, etc.), it is necessary to determine the absorption by the plain solvent as well as by the solution.

Determination of Extinction-coefficient.—This is, in principle, the same as in Glan's instrument, the operator making alternate substitution of tubes containing respectively the plain solvent and the solution. The absorption of the former is therefore automatically compensated; one obtains the extinction of the solute from the two following measurements:—

I. Solution in ray-bundle I, solvent in II, angle of Nicol α_1.

II. Solution in ray-bundle II, solvent in I, angle of Nicol α_2.

Suppose the solvent reduce the light from I′ to I″, then—

$$\text{(in I.)} \quad \frac{I_2''}{I_1'} = \tan^2 \alpha_1 \qquad \text{(in II.)} \quad \frac{I_2'}{I_1''} = \tan^2 \alpha_2$$

hence

$$\frac{I_2'}{I_1''} \cdot \frac{I_1'}{I_2''} = \frac{\tan^2 \alpha_2}{\tan^2 \alpha_1}$$

If ϵ is the extinction-coefficient of the solution, ϵ_0 that of

[1] Upper and lower in the diagram correspond to right and left in the instrument.

the solvent, and d the thickness of the absorbing substance in cms., then—

$$\epsilon - \epsilon_0 = \frac{\log \tan a_1 - \log \tan a_2}{d}$$

By using the two tubes alternately, the loss due to reflection (*vide* p. 140) is also compensated. If two tubes with different thicknesses of the same fluid are measured as above, the absolute value of the extinction-coefficient for the solution or solvent *per se* may be similarly obtained.

The chief objection to the König-Martens photometer is its small light intensity, owing to the splitting-up of the original beam into so many components. It will be seen that the field employed has at the most, apart from internal reflections and absorptions, only one-eighth of the intensity of the original beam. In this respect Hüfner's form is the best of the polarizing instruments.

The greatest sensitiveness in photometry is reached when the dividing line vanishes at equal brightness for the two fields. This condition is most perfectly realized by the cube devised by Lummer and Brodhun (p. 32), who have adapted it for spectrophotometric measurements.[1] In their instrument also the Maxwell observation method is employed. Two collimators at right angles to each other make two spectra, which are brought into contiguity by the cube. The measurements are made by means of the Vierordt slit method, supplemented by the use of a revolving sector.

Brace's Spectrophotometer.[2]—This is a simplification of Lummer and Brodhun's instrument, in which the dispersion prism is at the same time very ingeniously made to act as the contrast head.

The prism P consists of two separate halves. The bisecting surface of the half turned toward the observation tube R is silvered, with the exception of a strip removed in the centre in a direction perpendicular to the slit. The two halves are

[1] *Zeitschr. f. Inst. Kunde*, **12**, 132 (1892).

[2] D. B. Brace, *Phil. Mag.*, [5] **48**, 420 (1899).

cemented together, so that the reflected and transmitted bundles form two exactly contiguous spectra, the division line vanishing at equal brightness. Brace points out that when this line is visible the sensitiveness is reduced to at least one-half; the boundary is most noticeable in the Glan and Vierordt instruments, is practically negligible in the Hüfner and Martens instruments, but is completely absent in the Lummer and Brodhun head. However, in the photometry of absorptions two other factors have to be considered. These are the constancy and homogeneity of the original light-source. With respect to the first, in the Vierordt, Glan, Hüfner, and König instruments the same light-source illuminates two contiguous slits, the Martens illuminating apparatus making a still further refinement. In Lummer and Brodhun's, and in Brace's type of spectrophotometer the same light-source may be brought by reflecting systems to illuminate both slits.[1] Crova[2] used for his photometer two gas flames, fed on a T-branch from the same supply.

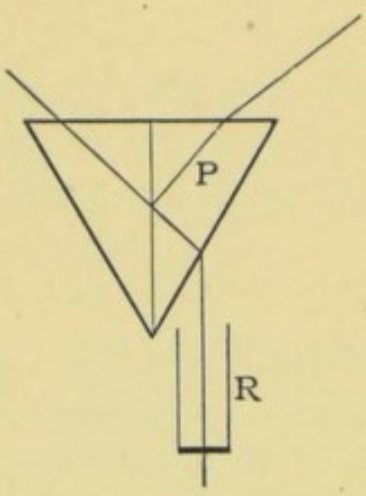


FIG. 13.

Brace uses the Vierordt method of altering one slit-width, but calibrates the slit optically first, so as to obtain from the slit readings the true optical values for different slit-widths and different colours. This calibration may be conveniently performed with a revolving sector. But whenever white light is used (this applies, of course, to all the instruments discussed), there remains an error due to the lack of homogeneity of the light-source. Even with a very fine collimator slit, and an ocular slit as narrow as possible, the finite width of the former produces a mixed colour, while the ocular slit allows a *definite* region of the spectrum to pass. Suppose the collimator slit be 0·10 mm., and the ocular slit 0·25 mm. in width, the spectral

[1] B. Moore, "Spectrophotometry of Copper and Cobalt Solutions," *Phys. Rev.*, **23**, 321 (1906).

[2] *Ann. de Chim. et phys.*, [5] **29**, 556 (1883).

regions on the limits of the ocular will differ by some 4 $\mu\mu$,[1] whilst if the collimator slit has to be widened the spectral band becomes impurer. When the curve of an absorption is not very steep, the error is not great, but if the absorption is varying rapidly with wave-length, then on the one hand the field, even for a narrow ocular slit, is not evenly illuminated, and at the same time, the value of the extinction coefficient depends on the slit-width; the following table from Martens and Grünbaum illustrates this.

Substance.	Wave-length in mm.	Breadth of collimator slit.	ϵ for Welsbach	ϵ for homogeneous.
Aqueous solution of dinitrosulphonic acid . .	508·5	0·75	0·343	—
	508·5	0·25	0·364	—
	508·5	immaterial	—	0·378
Aqueous solution of K_2CrO_4	508·5	0·33	0·292	—
	—	0·075	0·305	—
	—	immaterial	—	0·318
Fuchsine in alcohol . .	593·94	0·10	0·0589	0·0624
	589·0	0·10	0·0924	0·0983
	577·579	0·10	0·252	0·284

To avoid this, Martens and Grünbaum, and Müller,[2] use homogeneous light of spectral lines. For the method of obtaining these, their papers must be consulted.[3] A mixture of helium and hydrogen, with a little mercury vapour, in a Plücker tube, as recommended by Collie, is specially useful. With respect to this method, it must be noticed (*a*) that the intensity is low, which is to some extent compensated for by the possibility of using a very wide slit. Also a wavering or inconstant source for any line lowers the sensitiveness; and (*b*) small variations in the form of absorption-curves may be overlooked. Whilst valuable for absolute measurements, the use of a continuous spectrum, with a fixed slit-width, is to be recommended for the comparison of, say, the relative

[1] Martens and Grünbaum, *loc. cit.*, p. 993; P. Vaillant, *Ann. de Chim. et Phys.*, [7] **28**, 213 (1903).

[2] E. Müller, *Ann. Phys.*, [4] **21**, 515 (1906).

[3] See also E. C. C. Baly, *Spectroscopy*, p. 364.

intensities in a banded spectrum. (*c*) This method is not sufficiently elastic for the application of spectrophotometry for quantitative analysis.[1]

Brace Spectrophotometer.—An improved form of this has been worked out by R. J. Wallace, in a form also suitable for the measurement of photographic densities,[2] in which a polarizing prism is used to alter the light strength of the comparison field.

Measurement of Absorptions.—Vessels for the spectroscopic examination of solutions vary of course with the nature of the investigation;[3] for spectrophotometry the solution is usually placed in a parallel-walled glass vessel, of 11 mm. diameter, in the lower portion of which is a glass cube, of exactly 10 mm. thickness; hence the extinction is measured for a layer 1 cm. thick, and the reflections from the solution are automatically compensated.[4] The use of tubes, with illumination by strictly parallel light, enables greater lengths and thereby greater dilutions to be measured. Müller[5] has devised a special form of tube in which the solution is kept at a constant adjustable temperature by an electric current passing through a wire-spool wound about the tube. A plane-parallel quartz cell, and also a wedge-shaped cell for the examination of absorption-spectra are described by H. C. Jones and his co-workers.[6] A form suitable to the older type of König instrument (where the collimator slits are one above the other) has been described by V. Henri.[7]

[1] Cf. Krüss, G. and H., *Kolorimetrie und Quantitative Spektral Analyse*, pp. 116, 149 (1891), on the similar question as to the validity of Beer's law.

[2] *Astrophys. Journal*, **25**, 116 (1907).

[3] Cf. Baly, *Spectroscopy*, p. 414.

[4] Cf. Krüss, *loc. cit.*, p. 100.

[5] *Ann. de Phys.*, [4] **21**, 518 (1906).

[6] H. C. Jones and H. S. Uhler, *J. Am. Chem. Soc.*, **37**, 124 (1906).

[7] *Compt. Rend. Soc. Biol.*, T. **61**, 743 (1906).

CHAPTER III

THE ENERGETICS OF RADIATION

§ 21. The Emission and Absorption of Light.

We have seen at the commencement that light is one form of radiant energy, also that it may arise from a variety of transformations of energy, and again be retransformed into any one of these. The first process is the *emission* of light, the second its *absorption*. For one form, viz. the mutual transformations of light and heat, very definite laws have been obtained. Every substance above absolute zero (-273° C.) radiates energy at the cost of its own heat energy. Such radiation has been termed "pure temperature" radiation (R. von Helmholz), since it depends only on the temperature of the body. When it is due to electrical or chemical processes, in part or entirety, then the phenomenon is termed *luminescence* (E. Wiedemann). An example is the case of phosphorescence. The former process can be successfully treated thermodynamically;[1] some of the results are briefly dealt with here. The advance made in the quantitative examination of radiation phenomena has been uncommonly well balanced, inasmuch as the experimental and measuring side has developed *pari passu* with theoretical analysis.

§ 22. Emissivity and Absorption Power.

When we pass from the photometric determination of light intensities to the measurement of the energy radiated by its heating power, the question of time is involved. The *specific*

[1] See F. G. Donnan, *Thermodynamics*, this series.

emissivity or *emission power* of a substance, at a temperature T and for wave-length λ, is the energy radiated by unit surface in unit time. We shall term this e_λ, the total emissivity of the whole surface being E_λ. For a radiation between λ_1 and λ_2, the emissivity $E_{\text{lim 1}}^{\text{lim 2}} = \int_{\lambda_1}^{\lambda_2} E_\lambda d\lambda$, and the total emissivity over the whole spectrum—

$$E = \int_0^\infty E_\lambda d\lambda$$

Radiation Equilibrium.—In an enclosed system into which no heat can penetrate (adiathermic), let there exist bodies at different temperatures; then the temperature will ultimately reach a constant value, not merely by the warmer bodies radiating heat to the cooler, but by a mutual exchange, each body simultaneously radiating and absorbing heat according to its temperature and specific constitution, but independently of the radiation incident. The constant temperature of the system is due, not to a static condition, but to a dynamic equilibrium of radiation; this view is due to Prévost.[1] According to this view, a body is not solely radiating heat when its temperature is falling, or solely absorbing when its temperature is rising, but both processes are occurring simultaneously, the radiation depending only on the body itself, the absorption on the nature of the body and the condition of surrounding bodies. It will be seen that this temperature equilibrium is essentially dynamic, so that the conception is similar to that of chemical equilibrium.[2]

The Absorption Power.—By this is understand the relation of the intensity of the radiation absorbed by a body to that incident upon it. Suppose I_0 be the intensity of the incident radiation, I that which is transmitted, then disregarding reflection, $I_0 - I$ is absorbed, and the absorption power is $\frac{I_0 - I}{I} = A$.

[1] Prévost, *Sur l'équilibre du Feu* (Geneva), 1792, *Journ. de Phys.*, 1811; cf. T. Preston, *Theory of Heat*, p. 440.

[2] Cf. Mellor, *Chemical Statics and Dynamics*.

The Relation of Emission Power and Absorption Power. Kirchhoff's Law.—It was indicated by Balfour Stewart, and fully and independently enunciated by Kirchhoff,[1] that a very important relation exists between the emission and the absorption powers of bodies. The statement of this, which is known as Kirchhoff's law, is as follows:—

The value A can vary between 1 and 0. When a ray of light falls on a body, one part, A, is absorbed, another, R, is reflected, and another, D, transmitted. Hence, if we suppose the original intensity to be 1,

$$I_0 = A + R + D = 1$$

For gases, the reflection is practically nil, so that $A = 1 - D$, whilst for metals, except in very thin films, no light is transmitted, and

$$A = 1 - R$$

In some cases, R must be split up into two portions, the reflection from the surface, R_1, and internal reflection, R_2. Such is the case with heterogeneous systems like the silver bromide emulsion in photography. Here R_2 plays a very important rôle.

"The ratio between the emissivity or emission power for the same temperature and wave-length is the same for all bodies."

We have then, for any number of bodies independently of their nature—

$$\frac{E_1}{A_1} = \frac{E_2}{A_2} = \frac{E_3}{A_3} = S$$

What is the physical meaning of the constant S? If we put $A_\lambda = 1$, then $S_\lambda = E_\lambda$, i.e. *it is the emissivity of a body which absorbs all the radiation incident upon it, reflecting none.* Such a body was termed by Kirchhoff an *absolute black* body; it has been further proposed[2] to term the radiation from such, "black radiation."

[1] G. Kirchhoff, *Berl. Ber.*, 1859, p. 783; Ostwald's *Klassiker*, No. 100, 1898.

[2] M. Thiessen, *Verh. deutsch. phys. Ges.*, **2**, 37 (1900).

Kirchhoff's law may be theoretically deduced by the application of the second law of thermodynamics to the temperature equilibrium in an adiathermic enclosure.[1] An experimental proof, direct, has been made by Pflüger.[2]

Of qualitative illustrations many could be cited, but one given by Balfour Stewart will suffice. A dark enamel burnt in on porcelain shines more brightly on heating than the background.

§ 23. The Absolutely Black Body.

An exact test of Kirchhoff's law only became possible when the theoretical black body (A = 1) could be experimentally realized. No single substance fulfills the conditions, at any rate over a wide enough range of temperature. But there is implied in Kirchhoff's deduction of his law a method of constructing such a body.[3] For within an enclosed space, the walls impermeable to heat and of equal temperature, the radiation will be that of a black body, *i.e.* the radiation proceeding from any part of its surface to the centre, is the same as though the surface were completely "black," whatsoever its substance consist of. If a small opening be made, the radiation can pass out and is practically identical with that of the black body. For consider any body surrounded by the enclosure, which has been brought to constant temperature, then the mutual radiations of the body and the walls cannot alter the temperature. The body loses according to its emissivity E, but at the same time gains a fraction A of the heat e emitted by the walls. For equilibrium of temperature it follows that $E = eA$.

[1] Of numerous demonstrations, one of the clearest is that of E. Pringsheim, *Zeit. wiss. Phot.*, I., 360 (1904).

[2] *Drude's Annalen*, **7**, 710 (1902). This verification took special account of the polarization of the radiation. There have been numerous others.

[3] E. Pringsheim, in his deduction of Kirchhoff's law, inverts the latter's procedure, in that he deduces this law from the existence of "black" radiation in an enclosure of equal temperature. For the existence of a "black" body is the statement of the law of heat-radiation in plain physical terms. See *Zeit. wiss. Phot.*, **1**, 360 (1904).

If we suppose the walls to radiate the amount e, then they obtain back by reflection $e - e\mathrm{A}$, plus the radiation E of the body. Hence again—

$$e - e\mathrm{A} + \mathrm{E} = e$$

whence

$$\frac{\mathrm{E}}{\mathrm{A}} = e$$

NOTE.—It will be seen that the statement is essentially the same as for the solution and emission of a perfect gas in an indifferent solvent.

It has been shown by Bohr. (Drude's *Ann.*, **1**, 244 (1900)) that the transference of a gas from the gas-space to a liquid for a constant temperature and surface of the latter, and homogeneous convection by stirring, follows the law—

$$\frac{dx}{dt} = \mathrm{K} \,.\, \mathrm{C}_{\mathrm{gas}} - \mathrm{K}_1\mathrm{C}_{\mathrm{fl}}$$
$$= \mathrm{K}\left(\mathrm{C}_2 - \frac{c}{a}\right)$$

K and K_1 are the invasion and emission constants, whilst $a = \frac{\mathrm{K}}{\mathrm{K}_1}$ is Bunsen's absorption coefficient.

In the case of radiation we have $\mathrm{A} = \frac{\mathrm{E}}{\mathrm{S}}$. If radiations of different wave-length behaved independently, we should have a case precisely analogous to Henry's law of partial pressure, but radiation behaves as a *coherent mixture*, the correlation of its components (or equation of state) being the particular value of $\mathrm{S}\lambda$.

Following out this principle, experimental "black bodies" have been constructed by Lummer and Pringsheim,[1] who used a double-walled metal vessel kept, for example, in a constant temperature bath of molten saltpetre, or at the highest temperatures in a gas oven, and also by Paschen,[2] who used an electrically heated carbon filament in the middle of an internally reflecting sphere.

The importance of these experiments may be gauged by the fact that it became possible to test not only Kirchhoff's law, but all theoretical deductions as to the properties of "black radiation," whilst there is obtained at the same time an experimental normal furnishing "black radiation," if

[1] W. Coblentz, *Investigation of Infra-Red Spectra*, Carnegie Institute of Washington, 1905.

[2] *Wied. Ann.*, **60**, 719 (1896).

necessary above 2000°,[1] so that radiations can be compared both with standard "black" radiation and with each other.[2]

§ 24. The Radiation Function.

Kirchhoff himself stated that full value of his law would only be obtained when the form of the function could be experimentally found which was determining the radiation of the black body for every wave-length and every temperature. For pure temperature radiation, this law puts the emission of all bodies in simple relation to that of the black body.

We have expressed this law in the form $\frac{E_\lambda}{A_\lambda} = S_\lambda$, which gives us, when $A_\lambda = 1$, $S_\lambda = E_\lambda$. The function S_λ expresses the most general form possible of the relation of radiation to temperature and wave-length; it is the general radiation function, independent of the specific absorptive properties of individual substances. It gives at the same time the highest value which the radiation of a body can attain for a given temperature. But it must be borne in mind that we are only concerned with pure temperature radiation. How far thermodynamic considerations can be applied to the emission of light when this is due, in part or entirely, to chemical changes, will be discussed later.[3]

§ 25. The Stefan-Bolzmann Law.

The law relating the total radiation S of the black body to its temperature was empirically deduced by Stefan[4] from

[1] By the use of iridium as the material, W. Nernst, *Phys. Zeitschr.*, **4**, 733 (1903).

[2] The methods and instruments (bolometers, radiometers, radiomicrometers, etc.), for the measurement of radiation qua heat will be found discussed in *Spectroscopy*, E. C. C. Baly; K. Schaum, *Photochemie and Photog.*, Pt. I., p. 16. See also reports of the Physical Technical Reichsanstalt in recent years, *Zeitschr. f. Inst. Kunde* and *Zeit. wiss. Phot.*, 1900–1910.

[3] See Chapter VII.

[4] *Sitz. Ber. Wiener Akad.*, **79**, Abt. II. 391 (1879).

Dulong and Petit's[1] experiments on the rate of cooling of bodies. Stefan himself considered his expression a general law for all bodies, but Bolzmann,[2] obtaining the same expression by a thermodynamical application of the conception of the pressure of light, showed that it was only valid for black radiation. This is the law stated in words:

"The total radiation is proportional to the fourth power of the absolute temperature," or in symbols, $S = CT^4$, where S is the total radiation, T the absolute temperature, and C a constant.

Maxwell had shown that it followed from the electromagnetic theory of radiation that light should exert a pressure in the direction of transmission, numerically equal to the density of the energy. The same result was reached by Bartoli[3] by thermodynamic reasoning as to the work-capacity of radiation. Many attempts to measure the force exerted on a suitable light body suspended in a vacuum were defeated by the convection phenomena of the residual gas (Crooke's radiometer phenomenon). It remained for Lebedew[4] and Nichols and Hull,[5] independently in 1901, to demonstrate its objective existence, Lebedew obtaining results agreeing within 20 per cent. of theory, whilst Nichols and Hull by great refinement in method obtained agreement to within 1 per cent.

The Stefan-Bolzmann law was experimentally verified for the black body by O. Lummer and E. Pringsheim.[6] We can write it in the form—

$$S = C(T^4 - T_0^4)$$

where T is the absolute temperature of the radiating body, T_0, of the measuring body, S is the observed difference in

[1] *Ann. de Chim. et de Phys.*, 2e, tom. vii., 225, 337 (1817).

[2] *Wied. Ann.*, **22**, 291 (1884).

[3] *Wied. Ann.*, **47**, 479 (1892). See also Prince Galitzine, *Ann. d. Phys.*, **6**, 433 (1901).

[4] *Phys. Rev.*, Nov., 1901.

[5] *Astrophys. Journ.*, **17**, 315 (1903).

[6] *Wied. Ann.*, **63**, 395 (1897).

radiation of the two. The results obtained, using a surface-bolometer, are given in the table.

I.	II.	III.	IV.	V.
Observed abs. temperature.	Reduced heat of galvanometer.	$\gamma C \times 10^{10}$	Calc. abs. temp.	$T_{obs.} - T_{calc.}$
371·1	156	127·0	374·6	−1·5°
492·5	638	124·0	492·0	+0·5
723·0	3,320	124·8	724·3	−1·3
745·0	3,810	126·6	749·1	−4·1
810·0	5,150	121·6	806·5	+3·5
—	6,910	123·3	867·1	+0·9
—	44,700	124·2	1379·0	−1
—	57,400	123·1	1468·0	+2
—	60,600	120·9	1488·0	+9
1535·0	67,800	122·3	1531·0	+4
	Mean	123·8		

Column I. gives the thermometrically measured absolute temperature of the black body; Column II. the excursions of the galvanometer, which are directly proportional to the radiation; Column V. the temperature calculated for each observation, using the *mean* value *of* C. The values in Column V. show that the deviations are small and without bias. The constant C is a natural constant of great importance; its numerical value, according to Kurlbaum, is $5{\cdot}32 \times 10^{-5}$ ergs. per square centimetre per second. By its means the calorimetrically measured radiation of bodies can be used to calculate their temperatures.[1]

So much for the total radiation. We now have to consider the spectral distribution of the energy in its relation to temperature. The facts obtained experimentally (and theoretically) for black radiation are most easily expressed graphically. The accompanying curves show the results obtained by Lummer and Pringsheim for the distribution of energy in the normal[2]

[1] Cf. O. Lummer and E. Pringsheim, *Verh. deutsch. phys. Ges.*, **1**, 230 (1899); **3**, 36 (1901).

[2] A normal spectrum is one in which the distance between two spectral colours is proportional to the difference of their wave-lengths. See E. C. C. Baly, *Spectroscopy*, p. 35.

spectrum of the black body. Each curve relates to one tempe-

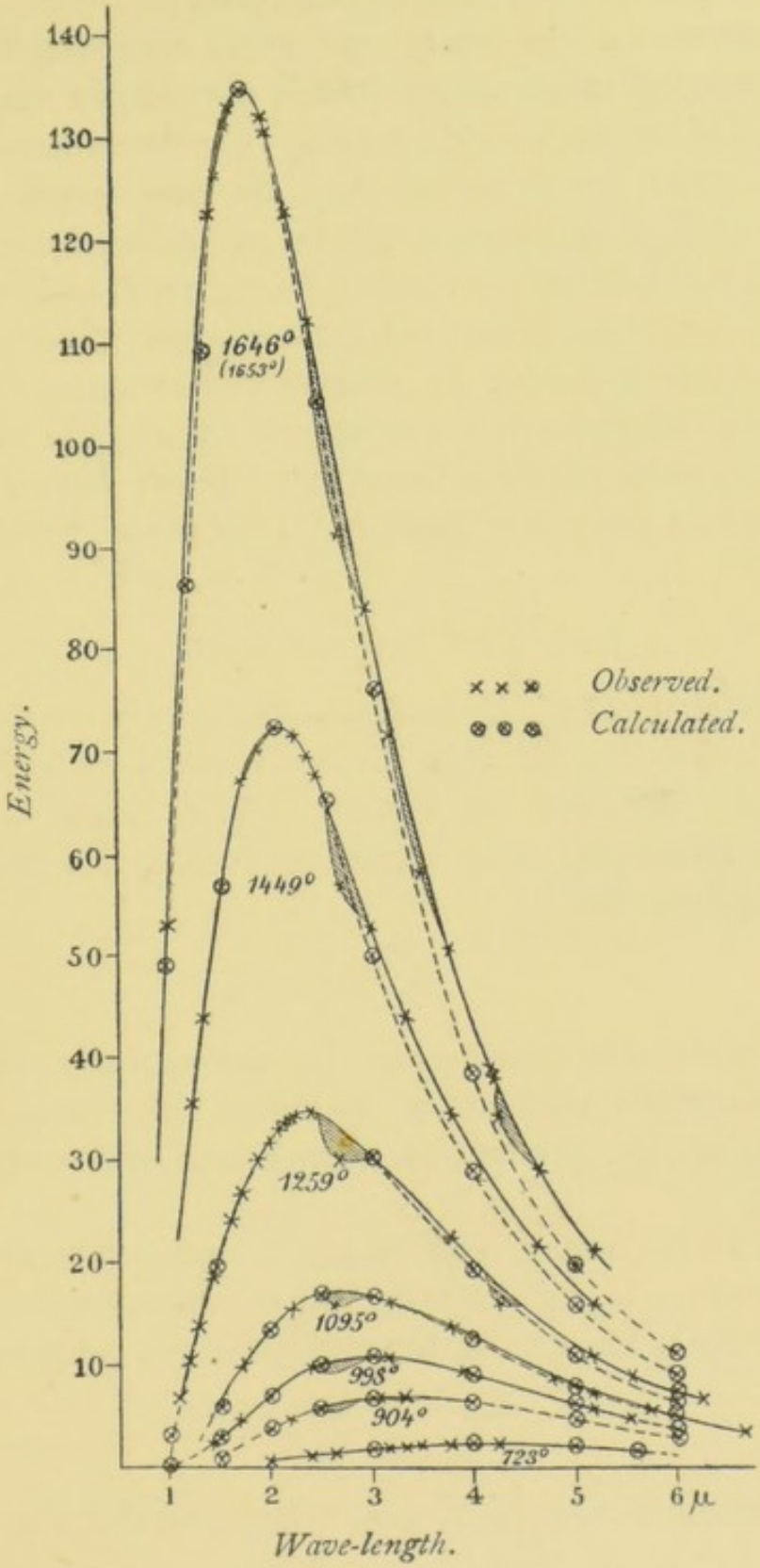


FIG. 14.

rature, that is, they are isotherms, the ordinates being proportional to the emissions, the abscissæ giving wave-lengths in μ.

A casual inspection reveals certain interesting properties. The curves never intersect, but each lies above one for a lower temperature, *i.e.* the energy of every wave-length increases with increased temperature. Each curve has a maximum, the energy diminishing on either side. The wave-length at which this maximum lies is termed λ_{max}, the corresponding maximal emissivity S_{max}. Further, it will be noticed that the position of λ_{max} lies for different curves in different parts of the spectrum, and, in fact, with rising temperature, the maximum is continually shifting toward the shorter wave-lengths, so that with increasing temperature the energy of the shorter wave-lengths increases more rapidly than that of the longer; thus an incandescent body first glows red, then passes to white heat.

§ 26. The Displacement Law.

W. Wien, in 1893,[1] by an application of Doppler's principle,[2] obtained the law for this displacement, previously deduced empirically in 1888 by Weber. Wien found the relation between colour and temperature involved in the shortening of wave-length to be—

$$\frac{\lambda}{\lambda'} = \frac{T'}{T}$$

that is, when the temperature increases, the wave-length of every monochromatic action radiation diminishes in such a manner that the product of temperature and wave-length is constant.

Weber's maximum relation $\lambda_{max}\, T = \text{constant}$ appears as a special case. If this relation be combined with the Stefan law, we obtain for the displacements the two relations—

$$\lambda_{max}\, T = A = 2940$$

and

$$S_{max} = BT^5$$

"The maximal energy is proportional to the fifth power of

[1] *Wied. Ann.*, **58**, 662 (1896).

[2] Change in vibration frequency observed when either the source or the observer is moving in the line of transmission. See E. C. C. Baly, *Spectroscopy*, p. 535.

the absolute temperature." The expression combining the Stefan law and Wien's displacement law, which may be written $S_{max} T^{-5}$ = constant, B, has been verified by many observers. The following table shows Lummer and Pringsheim's results.[1]

TABLE I.

Abs. temp.	λ_{max}	S_{max}	$A=\lambda_{max}T$	$B=S_{max}T^{-5}$	$T=\sqrt[5]{\frac{S_{max}}{B_{mean}}}$	$T_{abs.}-T_{calc}$
621·2°	4·53	2·026	2814	2190×10^{-17}	621·3°	−0·1°
723·0	4·08	4·28	2950	2166 ,,	721·5	+1·5
908·5	3·28	13·66	2980	2208 ,,	910·1	−1·6
998·5	2·96	21·50	2956	2166 ,,	996·5	+2·0
1094·5	2·71	34·0	2966	2164 ,,	1092·3	+2·2
1259·0	2·35	68·8	2959	2176 ,,	1257·5	+1·5
1460·4	2·04	145·0	2979	2184 ,,	1460·0	+0·4
1646·0	1·78	270·6	2928	2246 ,,	1653·5	−7·50
		Mean = 2940		2188×10^{-17}		

The constant A, like the constant of the Stefan-Bolzmann relation, is a natural constant, for radiation, independent of the particular conditions. The simplicity of the three relations obtained was foreseen by Kirchhoff, as a natural consequence that they express energy relations synthesized independently of the properties of particular bodies.

§ 27. THE SPECTRAL DISTRIBUTION OF ENERGY.

In the same memoir in which he deduced the displacement law, Wien formulated a general theory for the radiation of the black body. He made the special hypotheses—

(*a*) That every molecule in a gas sending out radiant energy emits vibrations of one wave-length only, which depends solely on the velocity v of the molecule.

(*b*) The intensity of the radiation contained between the wave-lengths λ and $\lambda + d\lambda$ is proportional to the number of molecules emitting radiation of that period.

[1] *Verh. deutsch. phys. Ges.*, 1, 23, 215 (1899).

The form of the emission function which Wien obtained was—

$$S\lambda = \frac{C}{\lambda^5 e^{\frac{c}{\lambda T}}}$$

where C and c are constants, e the base of natural logarithms. Wien's deduction, based on hypotheses interjected into the kinetic theory of gases,[1] was criticized by W. Michelson,[2] and though at first supported by experiments of Paschen[3] and by an independent derivation based on the electromagnetic theory of light by Planck,[4] was shown by Lummer and Pringsheim,[5] in a very careful experimental investigation, to fail increasingly as the value λT is increased. Working at first with a fluorspar prism their experiments extended to wave-length 7μ, and then with a sylvin prism to 18μ. The deviations are best exhibited graphically as follows. If Wien's equation holds, on plotting the logarithm of the emission for a given wave-length λ as ordinates, and the reciprocal value of the temperature $\frac{1}{T}$ as abscissæ, the curves obtained should be straight lines. Wien's equation may be written—

$$S_\lambda = C\lambda^{-5} \cdot e^{-\frac{c}{\lambda T}}$$

when $$\log S_\lambda = \log C - 5 \log \lambda - \frac{c}{\lambda T}$$

which for a constant wave-length λ becomes—

$$\log S_\lambda = K - \frac{K'}{T}$$

[1] See S. Young, *Stoichiometry*, pp. 185, 238 (Longmans, 1908); also P. Drude, *Lehrb. d. Optik.* (S. Hirzel, Leipzig, 1900), p. 482. In considering a mass of gas as a "black body," it must be remembered that it is only necessary to conceive a layer sufficiently thick to absorb all light when A = 1.

[2] Cf. A. L. Day and C. E. van Ostrand, *Astrophys. Journ.*, **19**, 16 (1904).

[3] *Berl. Ber.*, 405, 959 (1899).

[4] *Theorie d. Wärmestrahlung* (Leipzig, 1906 : J. A. Barth).

[5] *Drude's Ann.*, **6**, 192, 1901.

the equation to a straight line. Such curves are termed "isochromates" (Paschen), and it will be seen that the deviation from theory are most evident, amounting in the extreme to 60 per cent. of the observed values.

The deviations were confirmed by Rubens and Kurlbaum [1] for long wave-lengths up to 50μ obtained by the method of

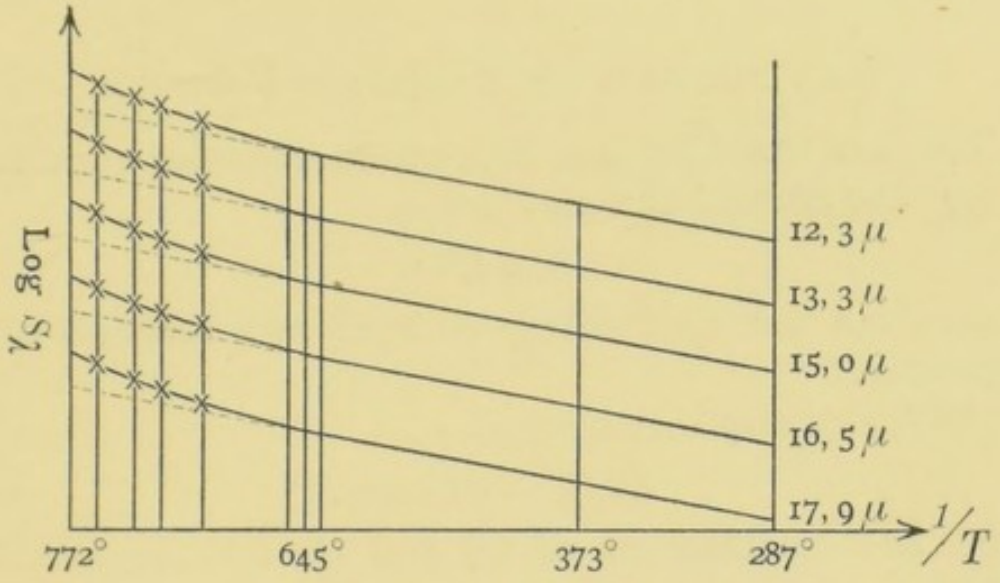


FIG. 15.—Isochromates.

residual rays.[2] Planck [3] now obtained a new spectrum-equation of the form—

$$S_\lambda = \frac{C}{\lambda^5(e^{\frac{c}{\lambda T}} - 1)}$$

C and c are two constants, of which C depends on the experimental condition; c has, however, always the value 14,600. It stands in simple relation to the constant A of the displacement equation $\lambda_{max}T = A$, for—

$$c = 4{\cdot}965A$$

and as A has the value 2940, we have—

$$c = 14{,}600$$

It will be seen that this only differs from Wien's by the term -1 in the denominator. For fairly small values of λT,

[1] *Drude's Ann.*, **4**, 649 (1901).
[2] See E. C. C. Baly, *Spectroscopy*, p. 243.
[3] *Drude's Ann.*, **7**, 716 (1900); **4**, 553 (1901); **6**, 818 (1901).

the difference in numerical values given by the two formulæ are not important. For $\lambda T = 3000$, the value of $e^{\frac{c}{\lambda T}} = 130$, and the subtraction of 1 would not alter S_λ by 1 per cent.

Planck's formula has been found satisfactory for nearly all the experimental results obtained, and may be considered as adequate.

§ 28. Summary of Radiation Formulæ.

The laws found for pure temperature radiation are thus—

(*a*) The Stefan-Bolzmann law—

$$S = CT^4$$

which gives the total energy emitted as a function of the temperature.

(*b*) Wien's displacement law—

$$\lambda_{max} T = \text{constant.}$$

(*c*) The combination of (*a*) and (*b*) for the maximum energy—

$$S_{max} T^{-5} = \text{constant.}$$

(*d*) Planck's law for the distribution of energy in the spectrum. This is—

$$S_\lambda = \frac{C}{\lambda^5 (e^{\frac{c}{\lambda T}} - 1)}$$

but for values of $\lambda T > 3000$, Wien's form is sufficient. All equations must fulfil the conditions that at every temperature $S = 0$ when $\lambda = 0$ and $\lambda = \infty$, i.e. at every temperature, *all* wave-lengths are emitted.

These laws are true for "black" radiation. For non-black bodies, to which of course all ordinary light-sources belong, the position may be summarized as follows. If the bodies can be considered as "grey," that is, equally reflecting, then the energy equations hold, but with different values to the constants.

(*a*) The total emission increases with a power a of the absolute temperature, in general greater than 4, and dependent on the bodies' special nature.

(*b*) Increasing temperature shifts the maximum towards the shorter wave-length, so that—

(*c*) $$\lambda_{max} T = \text{constant}$$
$$S_{max} T^{a+1} = \text{constant}$$

(*d*) The energy-curve has the same form as for the black body, as far as Paschen's observations on platinum, iron oxide, copper oxide, lamp-black, and carbon show. Bodies with selective absorption naturally show particular deviations.

In this connection, it may be remarked that where a properly constructed "black body" is not at hand, or at least when such a degree of accuracy is not necessary, thin platinum foil coated with iron oxide, heated electrically, can be advantageously used as a radiator.[1] If one half be coated with the iron oxide, the other with any substance the emission of which it is desired to test, then the radiation of the latter can be compared, either spectrophotometrically or spectrographically, with that of the black radiator. The image of the glowing strip is projected on the slit of the spectroscope. The strip is so arranged that there is a rapid temperature fall from the centre; thus two spectral mounts are obtained, representing the respective spectral distributions of the intensities of the radiations.[2]

§ 29. Methods of Determining Temperature.[3]

The thermo-optical methods of pyrometry can only be briefly indicated here; for full information the student is referred to the authorities cited in the footnote. Methods may depend upon the use of the bolometer or other radiometer, or the photometer, or of both combined.

Their importance for photo-chemistry lies chiefly in the

[1] W. von Bezold, *Ann. Phys.*, **21**, 175 (1884).

[2] K. Schaum, *Sitz. ber. Marburg*, **7**, 156 (1907).

[3] C. W. Waidner and G. K. Burgess, *Phys. Rev.*, **19**, 422 (1904); also *Bull. Bur. of Standards*, Washington, **2**, 189 (1905); H. Le Chatelier and O. Boudouard, *Mesure des températures élevées*, Paris, 1900 (Carré et Naud), and extended English trans. by G. K. Burgess, New York (Wiley & Sons); London (Chapman & Hall), 1904.

determination of the energy curve of the light-source and the absolute measurement of radiant energy.

The purely thermal methods depend upon the calibration of a suitable radiometer with a black body of known temperature. The temperature of the source under examination may then be found.

(*a*) From the total radiation by means of the formula—

$$S = C(T^4 - T_0^4) \text{ (see p. 57).}$$

(*b*) From the maximum energy by Wien's relation—

$$S_m = BT^5$$

$$T = \sqrt[5]{\frac{\phi_m}{B} + T_0^5}$$

where ϕ is the galvanometer throw, and T_0, as before, the temperature of the bolometer.

(*c*) From the wave-length of maximum energy, when $T = \frac{2940}{\lambda_m}$, the energy curve being plotted from bolometer determinations.

(*d*) From the ratio of the energies of two given spectral regions. These are best taken within the region where Wien's equation is valid, since the calculations are thereby much simplified; under these conditions, if S_{λ_1} and S_{λ_2} are the bolometrically determined energies for two wave-lengths (practically, narrow spectral regions) λ_1 and λ_2, then—

$$T = \frac{c\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)\log e}{\log \frac{S_{\lambda_1}}{S_{\lambda_2}} - \frac{\log \lambda_2^5}{\log \lambda_1^5}}$$

But this method is usually carried out optically, in that instead of determining the ratio of the energies by a radiometer, we compare the ratio of the intensities for two narrow spectral regions by means of the spectrophotometer. Then we have—

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} = \frac{S_{\lambda_1}}{S_{\lambda_2}}$$

and substituting in Wien's formula—

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} = e^{\frac{c}{\lambda}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} = e^{K_1\left(\frac{1}{T_0}-\frac{1}{T}\right)}$$

or
$$\log \frac{I_{\lambda_1}}{I_{\lambda_2}} = K_1\left(\frac{1}{T_0}-\frac{1}{T}\right)\log e = K_2\left(\frac{1}{T_0}-\frac{1}{T}\right)$$

Hence
$$T = \frac{K_2}{\frac{K_2}{T_0} - \log \frac{I_{\lambda_1}}{I_{\lambda_2}}}$$

Where T_0 is the temperature of the standard black body used as comparison light-source, and $K_2 = \frac{c}{\lambda}\log e$

or it may be used in the form [1]—

$$\log T = K' - K_2 \frac{1}{T}$$

$$\text{where } K' = \log (C_\lambda^{-5})$$

$$K_2 = \frac{c}{\lambda} \log e$$

the value of the constants being obtained graphically by plotting the monochromats. As K' and K_2 do not depend on the temperature, if the logarithm of the intensity of a small strip of the spectrum is plotted for various temperatures, a straight line is obtained for log I against $\frac{1}{T}$, the inclination of which depends only on K_2.[2]

Owing to the sensitiveness of photometric measurements this method is of great practical value; for such short wave-lengths as those of the visible spectrum, the Wien formula holds to temperatures up to 5000°.

Another photometric method consists in measuring the increase in brightness of broad spectral regions, or of the total intensity, as the temperature is increased. It has been found

[1] The logarithms are Brigg's logs, to base 10.

[2] Paschen and H. Wanner, *Berl. Ber.*, 1899, p. 5; H. Wanner, *Ann. d. Phys.*, **2**, 141 (1900); O. Lummer and E. Pringsheim, *Verh. deutsch. phys. Ges.*, **3**, 36 (1901) have applied this method to the determination of the temperatures of electric glow-lamps for different current strengths.

for the black body that for these the following relation holds [1]:—

$$\frac{I}{I_0} = \left(\frac{T}{T_0}\right)^x \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where I and I_0 are the intensities at the temperatures T and T_0 and x is a function of T decreasing rapidly as this increases. E. Rasch finds that—

$$xT = K \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

when differentiating (*a*) above, he gets—

$$\frac{dI}{I} = K\frac{dT}{T^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

for the dependence of the optical intensity on the temperature of the radiator. At the same time he points out the resemblance of this to van 't Hoff's equation for the reaction-isochore [2]—

$$\frac{dK}{K} = -\frac{q}{R}\cdot\frac{dT}{T^2}$$

Now I, the luminosity, is a measure of the physiological sensation, and a function of the photo-chemical effect on the retina, so the parallelism is of considerable interest. Integrated, we have the equation—

$$\log I = C - \frac{K}{T}$$

which gives the same law as by applying Wien's expression directly for monochromatic radiation. Schaum [3] suggests that the applicability to broad spectral regions probably depends on the fact that in general in the alteration of brightness by temperature change, it is the spectral region of maximum sensitiveness for the eye which is the determining quantity.

[1] O. Lummer and F. Kurlbaum, *Verh. deutsch. phys. Ges.*, **2**, 89 (1900); O. Lummer and E. Pringsheim, *Phys. Zg.*, **3**, 97 (1901); E. Rasch, *Drude's Ann.*, **14**, 193 (1904).

[2] See J. Mellor, *Chemical Studies and Dynamics*, p. 384.

[3] *Photochemie u. Photophysik*, p. 41 (1905).

§ 30. The Radiation of Flames.

In ordinary sources of light the radiation proceeds from glowing carbon particles. In applying the laws of radiation to these it is assumed that their emission lies, as experimentally found for lamp-black, between that of the "black body" and of naked platinum.[1] Hence, by taking for λ_{max} T the values 2940 and 2630, an upper and a lower limit can be obtained for the temperature. The value λ_{max} is obtained from the bolometrically determined energy curve, and T then lies between—

$$\frac{2940}{\lambda_{max}} \quad \text{and} \quad \frac{2630}{\lambda_{max}}$$

The following table shows some results obtained for ordinary light-sources :—

Table II.

	λ_{max}	T_{max}	T_{min}
Arc lamp	0·7μ	4200° abs.	3750° abs.
Nernst lamp	1·2	2450 ,,	2200 ,,
Gas	1·2	2450 ,,	2200 ,,
Glow-lamp	1·4	2100 ,,	1875 ,,
Candle[2]	1·5	1960 ,,	1750 ,,
Acetylene[2]	1·0	3000 ,,	2700 ,,

§ 31. "Black" Temperatures.

The results of this "method of limits" may be compared with those obtained by considering the light-source as a "black body" (which it is not) and determining by the spectrophotometer its "black" temperature,[3] that is, not its true absolute

[1] O. Lummer and E. Pringsheim, *Drude's Ann.*, **14**, 34 (1904).

[2] Later determinations by Kurlbaum and G. Stewart (*Phys., Zg.* **4**, 1 (1901)) show that carbon particles in flames generally possess a more selective emission than platinum, so that the value will not lie between the limits given. For acetylene Nichols found the temperature T = 2137° abs. directly, and Stewart 1·05 for λ_m, so that $\lambda_m T = 2282$.

[3] L. Holborn and F. Kurlbaum, *Drude's Ann.*, **10**, 225 (1903).

temperature, but that lower value which a black body should possess to give the same intensity of radiation as the substance in question. By determining this, values are obtained which lie between the bolometrically obtained values.

If the black temperature of an incandescent body is determined for different wave-lengths, it may be concluded from the results whether the body in question possess selective emission or behaves as a "grey" substance (*vide* p. 64). This is most easily performed in the visible region, as follows.[1] The image of a horizontal filament in incandescence of the substance is thrown on the slit of a spectrophotometer, and at the same time that of a glowing black body which is directly behind it. There is seen the spectrum of the black body crossed by a narrow spectrum of the filament. By regulating the temperature of the black body the intensities of both for a given wave-length λ in both spectra are made the same, when the thermo-electrically determined temperature of the black body gives the black temperature of the filament for that particular intensity of λ; at the same time, if the spectrum of the filament on either side is at first darker, then brighter, then it possesses selective emission for the wave-length λ. The method can be made quantitative, and from the isotherms the nature of the selective emission is at once evident. Thus the Nernst lamp has a strong selective emission at $\lambda = 520\ \mu\mu$. The relations between the "black" temperature and the true temperature of a radiator have been discussed by L. Holborn and F. Henning[2] and by R. Lucas.[3] It is found that the following expression holds:—

$$\frac{1}{T_b} = \alpha \frac{1}{T} + \beta$$

where T_b = black temperature, and T the true temperature. This was found valid for glowing platinum.[4]

[1] F. Kurlbaum and G. Schulz, *Verh. deutsch. phys. Ges.*, **5**, 428 (1903).

[2] *Sitz. Ber. Akad. Berl.*, 311 (1905).

[3] *Phys. Zeit.*, **6**, 418 (1905).

[4] Quantitative spectro-photometric comparisons of the emissivities of solid and liquid selective (metal) radiators with that of a full radiator (black body) are now being made. For solid and liquid gold, see

§ 32. Radiation Scale of Temperature.

The absolute scale of temperature defined by Kelvin[1] is based on thermo-dynamics,[2] and should be independent of the particular properties of any substance. The ratio of any two temperatures on this scale is equal to the ratio of the quantities of heat taken in and given out by a reversible engine working between these limits. A theoretically perfect gas would fulfil the conditions, but all gases depart more or less from the theoretical behaviour.[3] Actually, however, the practical scale is taken from gas thermometers. But as Lummer and Pringsheim[4] have shown, it is possible to found on the laws of black radiation an independent absolute scale of temperature. If we define the absolute temperature from the radiation laws, for example, as proportional to the fourth root of the total radiation, we obtain a theoretical radiation scale, which moreover is practically realizable to 2300° abs., whilst the gas scale fails above 1420° abs.; above this recourse has to be made to extrapolation.

Any of the fundamental laws given above can be used to ground a method of temperature measurement. The constants C, A, and B were determined in the valid range of the gas thermometer, and, since the laws connecting them are to be considered as "laws of nature," they can be used outside this range. Beside the laws themselves, relations following from the spectral equation of Planck may be used. To make the readings of the new scale congruous with those of the thermodynamic and gas scales, the temperature interval between the freezing and boiling points of water may be divided into 100°; or, in order that the definition may be independent of any particular substance, let it be granted that the energy contained in one cubic centimetre of black radiation of the absolute

C. M. Stubbs, *Proc. Roy. Soc.*, A. **87**, 451 (1912); for solid and liquid copper and silver, C. M. Stubbs and E. B. Prideaux, *ibid.*, A. **88** (1913).

[1] *Phil. Mag.* 1848, or T. Preston, *Theory of Heat*, p. 615.

[2] See F. G. Donnan, *Thermodynamics*, this series.

[3] S. Young, *Stoichiometry*, "Properties of Gases," this series, p. 185.

[4] *Verh. Deutsch. phys. Ges.*, **5**, 3 (1903).

temperature 1° be a certain magnitude. Then, according to Kurlbaum's measurements, the degrees of this scale will coincide with the Centigrade degrees, if this magnitude is fixed as $7{\cdot}06 \times 10^{-15}$ ergs.

§ 33. Radiant Energy in Absolute Mass.

On the assumption that radiant energy can be completely converted into heat, then by measuring the heat evolved in a suitable arrangement, we can determine the quantity of energy in absolute units. For very intense sources, *e.g.* the sun, this may be done by measuring the rise of temperature of water, enclosed in a lamp-blacked vessel. Modifications of this principle have been designed by Pouillet, K. Ångström, O. Chwolson and others,[1] and where used for determining the sun's radiation, the instruments are termed pyrheliometers. It is obvious that any sensitive radiometer can be used for absolute measurements, if the heat-capacity of the instrument, the loss by cooling, and the surface exposed are accurately known. K. Ångström [2] has applied a thermo-electric couple in constructing a very sensitive compensation pyrheliometer in the manner following.

The radiation falls on one of two equal blackened strips of platinum foil (0·0001 to 0·002 mm. thick), the other being brought to an equal temperature by a current, and the equality of temperature determined by a thermo-electric junction. In a stationary condition the increment of energy and the loss by radiation are just equivalent. The radiation falling on the whole strip is—

$$\theta = 0{\cdot}24\, i^2 r \ \frac{\text{g. cal.}}{\text{sec.}}$$

where r is the resistance of the strip, i the strength of current, 0·24 is the electrothermic equivalent.

Applications of the bolometric principle for absolute

[1] Pouillet, *C. R.*, **7**, 24 (1838), and see J. Scheiner, *Strahlung und Temperatur d. Sonne* (Leipzig, Engelmann), 1899, p. 18.

[2] *Wied. Ann.*, **67**, 683 (1899); *Phys. Rev.*, **1**, 365 (1893).

measurements have been made by F. Kurlbaum [1] and others, whilst the Boys' [2] radiomicrometer and Callendar's radiometer can also be employed.[3]

§ 34. Some Results and their Expression.

The absolute mass of radiant energy may be expressed either by the constant C of Stefan's law, or by $R_{100} - R_0$, *i.e.* the amount of heat in calories [4] which a black body of 1 cm.^{2} surface at 0° receives from a similar one at 100° in one second at 1 cm. distance. From this the constant C can be calculated. Table III. gives the results obtained in different experiments.

Table III.

Observer.	$R_{100} - R_0$	$C_{10^{12}}$
Dulong and Petit . . .	0·015 gram. cal.	1·08
Lehnebach	0·0152 ,,	1·10
Kundt and Warburg . .	0·014 ,,	1·01
Graetz	0·0150 ,,	1·08
Christiansen	0·0167 ,,	1·21
Kurlbaum	0·0176 ,,	1·28

Of these Kurlbaum's is probably the most reliable for the black body: $R_{100} - R_0 = 0{\cdot}0176$ gr. cal. = 73,100 ergs. The constant C allows us to calculate the absolute (total) emissivity of 1 cm.^{2} surface of the black body at any temperature. Thus at

T abs.	T Cent.	E abs.
373°	100°	0·02478 gr. cals.
273°	0°	0·00711 ,, ,,

The constant C is called the radiation constant or coefficient (*vide* p. 64).[5]

[1] *Wied. Ann.*, **65**, 746 (1898).

[2] See note p. 56, and E. C. C. Baly, *Spectroscopy*, p. 246.

[3] H. L. Callendar, *Chem. News*, **91**, 242 (1905).

[4] The calorie is the unit of heat, usually the $\frac{1}{100}$ part of the heat required to raise 1 gramme of water from 0° to 100°.

[5] For forms of registering heliometers, so-called actinometers, but actually thermometric, see Crova, *Annales de chim. et phys.*, V. Ser. **11**, 480 (1885); VI. Ser. **14**, 180 (1888).

§ 35. The Mechanical Equivalent of Light.

By this is understood the energy per second which the light-unit radiates horizontally on to 1 cm.^{2} at 1 cm. distance, reckoned in absolute units, and *only for the visible spectrum*. It will be seen that it is a quite arbitrary quantity, but from it may be deduced a useful conception, namely, the light-effect of a light-source, *i.e.* the relation of the energy in the visible spectrum to the total energy emitted. Measurements of this ratio have been made by O. A. Tumlirz, F. E. Rogers, K. Ångström, and others.[1] The method used by Tumlirz was to measure first the entire energy radiated horizontally by the given light-unit, in this case the Hefner lamp, and then to cut off the so-called heat rays by a water-screen. E. L. Nichols and W. W. Coblentz[2] used the same method for acetylene, also interposing a screen of a solution of iodine in CS_2, which absorbs the visible spectrum while allowing the infra-red rays to pass. They found that a water-screen only allows rays up to 1·8μ to pass; it follows that the principle of separation by water and iodine screens is not trustworthy. K. Ångström[3] also found that the water-screen did not effect a satisfactory separation. Instead, using two lamps of the same spectral character, he resolved the light of one into a spectrum, screened off the invisible radiation and united the remainder by a lens, the image being thrown on to a photometer. The unaltered light of the other was made photometrically equal to this, and then the two radiations were compared bolometrically. In this way he obtained results for the Hefner lamp, widely differing from those of Tumlirz. The total radiation was measured in absolute mass with his compensation pyrheliometer. The results for the Hefner lamp were as follows:—

Σ = total radiation at 1 meter on 1 cm.^{2} surface in gram-calories.

[1] See K. Schaum, *Photochemie u. Photophysik*, p. 61.

[2] *Phys. Rev.*, **17**, 267 (1903).

[3] *Phys. Zg.*, **3**, 257 (1902); *ibid.*, **5**, 456 (1904); and *Phys. Rev.*, **17**, 302 (1903).

Λ = energy of visible radiation.

The ratio $\frac{\Lambda}{\Sigma}$ = the light-effect.

The visible radiation, if expressed in gram. calories, gives the heat equivalent of light; if in ergs, the mechanical equivalent; taking the Hefner lamp as standard.

Observer.	Σ in gram. cals.	Λ in gram. cals.	Λ in ergs.	$\frac{\Lambda}{\Sigma}$
Tumlirz	$148{\cdot}3 \times 10^{-7}$	$361{\cdot}10^{-9}$	15·15	0·024
	$162{\cdot}0 \times 10^{-7}$	$356{\cdot}40^{-4}$	14·8	0·022
Ångström . . .	215×10^{-7}	$206{\cdot}10^{-9}$	8·65	0·0096

We can, of course, conceive of a "light-effect" for every specific photo-chemical reaction in conjunction with any particular source of radiation; it will always be the ratio of the radiation acting on the chemical system to the total radiation of the source. Thus the light-effect for the green-leaf synthesis would be quite distinct from that for the eye, and again different for the photographic plate.

The greater the "light-effect," the more efficient the light-source, but actually all light-sources in ordinary use possess but a low light-effect, their radiation lying chiefly in the useless infra-red. If ϕ be the total energy employed by the light-source per second, and S the total energy radiated per second, the greater $\frac{S}{\phi}$ is, the greater the efficiency.

Before discussing light-sources in relation to their general photo-chemical availability, some account must be given of the terminology to be used. The definitions of the quantities involved will depend to some extent on the point of view. If we consider light-sources in the physiological sense, we have (*a*) photometric magnitudes, but if we are dealing with energy-sources we have (*b*) energy magnitudes. Now, as has already been pointed out, in photometric quantities proper, the element of time is not involved, because the eye does not possess the property of accumulating intensity, but extricates

the capacity factor or perspective content. As Schaum[1] has pointed out, its behaviour could be represented by an actinometer or light-sensitive reaction in which the reaction-product is immediately removed, the active mass of the original substance being continually kept at a constant value. Stimulation of the retina is not analogous to the progress of a photo-chemical reaction, but to the formation of constant potential in a light-sensitive cell.[2]

But in the generality of photo-chemical reactions time is of course a factor necessary to be considered, and similarly it enters into the problem of the production of light as an economic question. Both from the general photo-chemical view point and from the economic one, the most stimulating way of looking at radiation is as a flow of energy, analogous to the flow of water or electricity. Not being concerned with illumination in the technical sense, we shall not deal here with such questions as the spatial distribution of the light, the cost of production, the efficiency, or the life of light-sources. This is a branch of applied photo-physics, of great practical importance, and which has only received a scientific footing since the foundation of the theory of radiation, and its experimental measurement as sketched in the foregoing chapter.

[1] *Photochemie u. Photograph.*, Tl. I. p. 82 (Leipzig, A. Barth, 1908).

[2] This statement of the independence of visual impressions of any time factor must be taken with reservation, in view both of the persistence and fatigue of vision.

TABLE OF TERMS DEFINING THE EMISSION AND RECEPTION OF LIGHT IN ONE HOMOGENEOUS MEDIUM, WHEN V THE VELOCITY OF LIGHT IS CONSTANT.

Quantities pertaining to the source, *i.e.* to the emission.

	Quantity (1).	Description.	Formula.	Unit.
	Absolute emissivity	Total energy emitted in unit time	$S\delta t$	Gm. calorie or erg
	Emissivity over given spectral range		$e_{\lambda_2}^{\lambda_1}$	
	Radiation-flux	Energy filling solid angle ω	$e^{\omega} = s\omega$	
	Radiation-density	Energy per unit volume of space	$\frac{4\pi S\delta t}{v}$	
Light	Light-intensity	Flux of light in given direction $x = \cos\phi$	I_x $I_x d\omega$	(Hefner) candle C. *c.p.*
Light	Light-strength	Variable according to object in question		
Light	Illuminating power			
Light	Spherical light strength	Total light emitted	$4\pi I$	Spherical candle C. sph.
Light	Total light flux	Light filling ω		*cp.*
Light	Surface brightness	Flux of light emitted by unit surface of source in $\perp^{ar}$ direction	$i = \frac{I}{s}$ s surface	$\frac{cp.}{cm^2}$

Quantities pertaining to the recipient surface, *i.e.* quantities received.

Quantity.	Description.	Formula.	Unit.
Radiation strength	Energy incident perpendicularly on unit surface at unit distance per unit time	$\phi = \frac{S}{4\pi}$	$\frac{\text{ergs}}{\text{seconds}}$
Radiation (correlative to illumination)	Similarly at distance r	$\phi_r = \frac{S}{r^2}$	
Amount of radiation	Same for surface F	$\frac{SF}{r^2}$	
Illumination (current density of light flux)	Light-flux incident on unit surface at distance r	$\Upsilon = \frac{I}{r^2}$	Candle meters. (Lux)C.M. or M.K.
Amount of light or insolation	Light-flux falling on surface F at distance r in unit time	$L = \frac{IF}{r_2}$	Candle-meter-seconds C.M.S.

As absolute unit of quantity of light, analogous to the calorie or the coulomb, the *lumen* might be taken provisionally as $l = I\omega t$, where I is the reciprocal of the mechanical equivalent of light, ω is a unit solid angle, t is a unit of time.

CHAPTER IV

§ 36. Economic and Energetic Relations of Actual Light-sources

The classification of light-sources is carried out on the basis of the terms given in the foregoing chapter. Considerable confusion prevails in regard to the terminology and standardization of data, and in particular as regards the relation of thermo-dynamic to luminous efficiency.[1]

The quantity $\frac{S}{\phi}$ may be termed the relative radiating power; it is frequently desirable, in dealing with photo-chemical reactions, to be able to calculate the total energy incident on the system, in order to obtain some idea of what may be termed the economy of the reaction, *i.e.* the proportion of energy which does chemical work.[2] $\cdot$ ϕ, the total energy in gram-calories per sec., may be reckoned in flame sources from the heat of combustion, in electrical sources from the electrical energy. If we assemble the symbols useful in dealing with the energies of light-sources, we have—

I = mean spherical light-intensity in HK or c.p.

Σ = mean spherical total radiation in gram-cals. per sec. on 1 sq. cm. at 1 metre.

Λ = mean spherical visible radiation in gram-cals., etc.

$S = 4\pi \cdot 100^2\Sigma$ = total radiation flux.

$L = 4\pi \cdot 100^2\Lambda$ = total visible radiation flux.

ϕ = total energy used in gram-cals. per sec.

and, derived from these last-mentioned quantities, ratios or

[1] P. G. Nutting, "The Luminous Equivalent of Radiation." Reprint No. 103, *Bulletin of the Bureau of Standards, U.S.A.*, vol. 5, No. 2 (1908), p. 261.

[2] Cf. A. Byk, *Zeit. phys. Chem.*, **62**, 465 (1908). That is, the "light-effect" of the particular light-source for that particular reaction. Byk terms it the "Ausnutzungs-faktor."

quotients which can be used to characterize a light-source from the economic standpoint; there is a great diversity at present in regard to the nomenclature adopted for these quotients,[1] and consequently considerable confusion and uncertainty in their use, but in the following the terminology proposed by K. Schaum[2] has been adopted. Thus we have the following derived values:—

$\frac{S}{\phi}$ = relative radiating power.

$\frac{L}{\phi}$ = effective value (Nutz-effect).

$\frac{\Lambda}{\Sigma}$ = light-effect (luminosity factor, *i.e.* a proportionality factor).

$\frac{\Lambda}{I}$ = mean spherical light equivalent, *i.e.* actual luminosity in HK or c.p.

$\frac{L}{I}$ = spatial light-equivalent (a space distribution coefficient).

$\frac{\phi}{I}$ = economy, *i.e.* energy per c.p. This ratio, that is, the energy in ergs per c.p., is frequently termed in English works on photometry, the *efficiency*, a term more appropriately reserved for the *ratio* of the *light-equivalent* of the standard or normal source, say the Hefner candle, to the *economy* of the source in question. Hence, the *efficiency* so characterized has the value $\frac{L_n}{I_n} : \frac{\phi}{I}$

The table on p. 80 indicates the values for the most important light-sources, but there are enormous discrepancies in some of the values recorded for the derived quantities.

The table is taken from Schaum;[3] the letters affixed to the numbers refer to the observers: W. for W. Wedding, N. for G. L. Nichols, H. for R. von Helmholz, V. for W. Volge, Å. for K. Ångström. Schaum concludes that at present an exact energetic comparison of the principal light-sources is not possible.

[1] Cf. K. Schaum, *Zeit. wiss. Phot.*, **2**, 1389 (904). [2] *Ibid.*, *loc. cit.*, p. 390.
[3] *Photo-chem. u. Photog.*, Pt. I., p. 149 (Leipzig: J. A. Barth, 1908).

TABLE IV.

Light.	I mean sph.	S	$\frac{S}{\phi}$	$\frac{L}{S}$	$\frac{L}{\phi}$	$\frac{A}{I}$
Acetylene . .	—	—	—	·055 (Å.)	—	$170 \cdot 10^{-9}$ for I horizontal
Gas, flat flame .	—	—	·085 (H.)	·015	·0013	—
Argand . . .	—	—	·120 (H.)	·016	·0019	—
Petroleum . .	13·2(W.)	3·39	·032(W.) ·182 (H.)	·009(W.)	·00029(W.)	$27 \cdot 1 \times 10^{-9}$ I mean sph.
Auer or Welsbach	52·3(W.)	2·76(W.)	·017	·010	·00018	$4 \cdot 4 \times 10^{-9}$ I sph. (W.) 105×10^{-9} I horiz. (W.)
Carbon filament	12·8(W.)	·811	·057(W.) ·75 (H.)	·060(W.) ·072 (H.)	·0034 (W.) ·054 (H.) ·070 (V.)	$19 \cdot 9 \times 10^{-9}$(W.) $38 \cdot 2 \times 10^{-9}$ (H.) 174×10^{-9} (N.)
Osmium . . .	31·4(W.)	·946	·081(W.)	·077(W.) ·023(H.)	·0062 (W.) ·076 (V.)	$18 \cdot 5 \times 10^{-9}$(W.) $66 \cdot 9 \times 10^{-9}$ (R.)
Nernst lamp .	113 (W.)	6·70(W.)	·131(W.)	·065(W.)	·0085 (W.) ·067 (V.)	$30 \cdot 4 \times 10^{-9}$(W.) $45 \cdot 9 \times 10^{-9}$ (V.)
Arc	400 (W.)	—	—	·08–·13	·0032 (W.)	$5 \cdot 2 \times 10^{-9}$(W.) 138×10^{-9} (N.)
Magnesium . .	—	—	—	·137	—	132×10^{-9} (N.)
Hefner . . .	1 (horiz.)	—	—	·0096(Å)	—	206×10^{-9} (Å.)
Sun	$3 \cdot 3 \times 10^{27}$	—	—	·38	—	125×10^{-9} 116×10^{-9}

§ 37. THE HEFNER LAMP.

The relation of the optical intensity of the Hefner lamp to that of other standards has already been mentioned (*vide* p. 24). As it is a reproducible standard—though not ideal—burning a liquid of definite chemical constitution, we can, by making a spectro-photometric comparison between it and another light-source, determine the distribution of energy in the visible spectrum of the latter, if we already know that of the Hefner. This has been determined in absolute mass by O. Tumlirz[1] and Kn. Ångström,[2] the latter's observations appearing more reliable (*vide* p. 75). Ångström determined the energy-values for small strips of the spectrum, where—

$$I_\lambda = \int_0^\lambda S_\lambda d\lambda$$

[1] *Wiener Ber.*, **112**, 1382 (1904).

[2] *Phys. Rev.*, **17**, 302 (1903); *Phys. Zeit.*, **5**, 456 (1904).

with the compensated pyrheliometer, and compared his results with those given by Wien's equation—

$$S_\lambda = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}}$$

Integrating over each of the small strips $d\lambda$, the values for the mean wave-lengths λ were obtained by the formula—

$$I_\lambda = c_1 \int_0^\lambda \lambda^{-5} e^{-\frac{c_2}{\lambda T}} d\lambda$$

$$= c_1 \frac{e^{-\frac{C}{\lambda}}}{C^4} \left\{ \left(\frac{C}{\lambda}\right)^3 + 3\left(\frac{C}{\lambda}\right)^2 + 6\left(\frac{C}{\lambda}\right) + 6 \right\}$$

where $C = \frac{c_2}{T}$. By the method of least squares, the values $c_1 = 0{\cdot}016$ and $C = \frac{c_2}{T} = 7{\cdot}85$ were obtained from the observations; the calculated results agreed well with those found. Ångström gives the following values for energies radiated by the Hefner burner horizontally at 1 metre :—

TABLE V.

Wave-length.	I_λ gm./cals.	Wave-length.	I_λ gm./cals.
$0{\cdot}78\mu$	$23{\cdot}6 \times 10^{-7}$	$0{\cdot}58\mu$	$3{\cdot}23 \times 10^{-7}$
0·76	20·6	0·56	2·37
0·74	17·9	0·54	1·69
0·72	15·2	0·52	1·17
0·70	12·8	0·50 [1]	0·78
0·68	10·6	0·48	0·50
0·66	8·74	0·46	0·30
0·64	6·99	0·44	0·17
0·62	5·53	0·42	0·09
0·60	4·27	0·40	0·05

For the total radiation

$$\Sigma = 0{\cdot}0000215 \ \frac{\text{sec.-cm.}^2}{\text{gm.-cals.}}$$

For total energy as light

$$\Lambda = 20{\cdot}6 \cdot 10^{-8} \ \frac{\text{sec.-cm.}^2}{\text{gm.-cals.}}$$

and the light-effect (*vide* p. 79) $= \frac{\Lambda}{\Sigma} = 0{\cdot}0096$.

[1] Values from $0{\cdot}50\mu$ are by extrapolation.

Further, E. Hertzsprung[1] has calculated the values of the energy, using Planck's equation—

$$S_\lambda = c_1\lambda^{-5}\left(e^{\frac{c_2}{T\lambda}} - 1\right)$$

Taking Stewart's[2] determination of the Hefner's temperature as 1825° abs., and $c_2 = 14{,}600$, this gives a value of $\frac{c_2}{T} = 7{\cdot}8$. (It is not necessary, however, to use Planck's formula; the values differ very slightly in the visible spectrum.) The results he compared with others obtained as follows: S. Langley[3] has measured the energy in the solar spectrum for different altitudes; E. Köttgen[4] has compared spectro-photometrically the intensity in the sun's spectrum with that in the Hefner's. Taking the intensity at $\lambda = 0{\cdot}59\mu$ as 1 in both, the quotient—

$$\frac{I_\lambda(\text{sun})}{I_{\cdot 59}(\text{sun})} : \frac{I'_\lambda(\text{Hef.})}{I'_{\cdot 59}(\text{Hef.})}$$

gives the relative spectral intensities of the sun and the Hefner. But since—

$$\frac{S_\lambda(\text{sun})}{S_{\cdot 59}(\text{sun})} = \frac{I_\lambda(\text{sun})}{I_{\cdot 59}(\text{sun})}$$

the values of $\frac{S_\lambda(\text{sun})}{S_{\cdot 59}(\text{sun})}$, obtained from Langley's measurements, divided by the foregoing quotient, will give the energy values in the Hefner spectrum. The values so obtained agree very well with those from Wien's equation, putting $\frac{c_2}{T} = 7{\cdot}8$, and also with those obtained by Ångström, which is only natural, since Ångström took the value of $\frac{c_2}{T} = 7{\cdot}85$. From an investigation by Ladenburg,[5] it appears that the value of $T_{abs.}$ obtained from this for the temperature of the Hefner flame is too high. No account is taken of the absorption in

[1] *Phys. Zeit.*, **5**, 634 (1904). [2] *Phys. Rev.*, **15**, 306 (1902).

[3] *Wied. Ann.*, **19**, 226, 384 (1883); see also C. J. Abbot, *Smithsonian Misc. Coll.*, **45**, 74 (1902).

[4] *Wied. Ann.*, **53**, 793 (1894).

[5] R. Ladenburg, *Phys. Zeit.*, **7**, 697 (1906).

TABLE VI.

I. $\lambda_{(\mu)}$	II. Energy in solar spectrum according to Langley.	III. $\frac{I_{(sun)\lambda}}{I'_{(Hef.)\lambda}} : \frac{I_{(sun)\,0\cdot59\mu}}{I'_{(Hef.)\,0\cdot59\mu}}$ according to E. Köttgen.	IV. II. : III.	V. Energy in spectrum of Hefner lamp. From IV. by multiplication by 3·7/622.* (*a*)	Calculated from Wien's formula— $c_2/T = 7{\cdot}8$. (*b*)	$c_2/T = 8{\cdot}7$. (*c*)
0·43	380	19·18	18·1	0·12	0·13	0·074
0·47	502	8·65	56·9	0·35	0·39	0·26
0·49	560	5·56	98·6	0·60	0·62	0·46
0·51	588	3·68	160	0·95	1·0	0·76
0·53	604	2·54	238	1·4	1·4	1·2
0·55	614	1·87	329	2·0	2·0	1·7
0·57	620	1·34	462	2·8	2·8	2·9
0·59	622	1·0	622	3·7	3·7	3·7
0·61	617	0·787	783	4·7	4·9	5·0
0·63	614	0·604	1020	6·1	6·2	6·7
0·65	603	0·449	1340	8·0	7·8	8·9
0·67	590	0·357	1650	9·9	9·0	11·5
0·69	568	0·306	1850	11·1	11·8	14·5

* In the sub-columns (*a*), (*b*), (*c*) of V. the value S_λ of the Hefner lamp for $\lambda = 0{\cdot}59\mu$ is set equal to 3·7.

the flame, and what is obtained is the "black" temperature. Ladenburg has determined both the emission curve of the Hefner and acetylene flames, and also the absorptions for different wave-lengths, by means of a quartz prism spectrometer and a linear thermopile. The total reflecting power compared with gypsum was very slight, only 1 per cent. The measured emissions divided by the corresponding absorptions give the "blackened" emission, from which the true value of λ_m was obtained, and hence the temperatures from the relation $\lambda_m T = 2940$, also by measurement of the "black" temperature with the optical pyrometer by Kurlbaum's method (*vide* p. 69). If T_b = black temperature of a flame at λ, T its true temperature, and A its absorption at this point, then—

$$\frac{1}{e^{\frac{c_2}{\lambda T_b}}} \cdot A = \frac{1}{e^{\frac{c_2}{\lambda T}}}$$

or

$$\frac{1}{T} = \frac{1}{T_b} + \frac{\lambda}{c_2} \log_e A$$

and from this the value 1694° abs. was obtained, or, correcting for reflection, 1704° abs. *But these "corrected" values must not be used to calculate the energy-distribution given by Wien's equation.* The actual "quality-value" $\frac{c_2}{T}$ used must be the one corresponding to the total emission curve. Hertzsprung[1] has reviewed the different $\frac{c_2}{T}$ values which may be assigned to the Hefner flame. Thus Ångström, assuming the mean error of his measurements to have the same *absolute* dimensions, calculates $\frac{c_2}{T} = 7{\cdot}85$. If, however, the error be assumed to be of same *relative* magnitude, the value of $\frac{c_2}{T} = 7{\cdot}58$. By combination of Langley and Köttgen's measurements he obtained the value $\frac{c_2}{T} = 8{\cdot}03$ for the region $0{\cdot}43\mu$ to $0{\cdot}69\mu$. If we take Ladenburg's determination of λ_m (uncorrected) as $1{\cdot}54\mu$, then from the relation $\lambda_m T$ we get T (uncorrected) = 1909° abs., which gives $\frac{c_2}{T} = 7{\cdot}65$. The best value for the visible spectrum appears to be still somewhat uncertain.

§ 38. Gas Flames as Light-sources.

Constancy.—By the use of a pure gas burning under specific conditions, very constant light-sources can be obtained. Bunsen and Roscoe,[2] in many of their experiments, used a coal-gas mixture of constant composition; they allowed this to issue from a single-hole burner of platinum, provided with a reservoir which served to regulate small pressure-differences. With screened burners,[3] in which only a small portion of the flame, say 1 mm., is used, considerable variations may occur in the pressure without affecting the intensity. Thus with a

[1] *Phys. Zeit.*, **5**, 634 (1907).

[2] *Pogg. Ann.*, **101**, 202 (1859).

[3] Sheppard and Mees, *Theory of Phot. Process*, p. 20 (Longmans, 1906).

screened acetylene burner, no change was observed in the photo-chemical effect when the pressure was varied from 4 to 6·5 cms. of water. Schaum states that gas-burners give a fairly constant light when the flame is kept to a constant height (6·75 cm.) by a pressure regulator, using a one-hole burner of 1 mm. aperture. All flame sources should be surrounded by a large enclosure to avoid atmospheric disturbances, and the light allowed to issue from a suitable opening.

The use of a pure gas is preferable to that of a mixture such as coal gas. Bunsen and Roscoe in their later researches [1] used *carbon monoxide*, burning under a minimal pressure-difference (estimated at 0·001 mm. water). This was fed at a constant rate to a burner of fairly large bore, 7 mm. wide. The intensity was found to be a linear function of the rate of supply of the gas. This they termed their *normal* flame. *Acetylene* can readily be obtained in a state of sufficient purity; the main condition is that the gas is not overheated, either in generating or in the burner. Acetylene of the desired purity, with a pressure constant to 1 per cent., may be obtained by using Thorne & Hoddle's "Incanto" generator.[2] The gas which is generated by water obtaining access to the carbide, first bubbles through the water in the gasholder and then through a special purifier, the pressure being registered by an oil manometer. For small intensities, 1 to 20 c.p. screened burners of the Naphey type may be used; for greater intensities up to 300 c.p., either larger Naphey burners or a special annular burner, but in any case water-cooled. This is very essential, as a prime source of variation is the formation of polymers of acetylene by heating, which then choke the burner with a deposit of carbon. The flame should never be turned down, *but burnt at full intensity* for the burner in question and completely extinguished. It was noticed (see p. 23) that the amyl-acetate and pentane flames were considerably influenced by the state and pressure of the atmosphere. These conditions

[1] *Pogg. Ann.*, **101**, 202 (1859); Ostwald's *Klassiker*, **38**, p. 38.
[2] Sheppard and Mees, *loc. cit.*

seem to influence naked flames as used in photometry more than when they are enclosed, as in photo-chemical experiments. Wildermann, who controlled his acetylene light by a Rubens thermopile, states that it kept constant to 1 per cent. over long periods; but where greater accuracy than this is required, the external conditions have to be considered. For acetylene as a secondary standard, see J. Violle.[1]

Temperature and Energy Curve.—These have been determined by E. L. Nichols,[2] Ladenburg,[3] and others. Ladenburg finds 2093° abs. for the temperature (uncorrected for reflection), 2111° abs. (corrected), from optical measurements, which agrees closely with that found directly by E. L. Nichols, T = 2118° abs. But according to Ladenburg it varies somewhat in different parts of the flame. The uncorrected value of λ_m was 1·21μ, the corrected value 1·39μ, but it does not appear worth while to deduce a value for $\frac{c_2}{T}$ to give the energy distribution in the visible spectrum, as Hartmann's[4] spectro-photometric calibration of two different flames on a Hefner standard point to a variation of the quality-value with the burner and other conditions. For values of the "light-effect," etc., see Table IV., p. 80.

§ 39. Incandescent Gas.[5]

The universally used Welsbach or Auer light offers in many cases a very convenient source, especially where one of small dimensions is not required. The *constancy*—apart from considerations of the pressure and composition of the gas, which have already been dealt with—is not very great, as the intensity of the mantle passes through a maximum and then

[1] See p. 23; also subsequent modifications, B. J. Wallace, *Astrophys. Journ.*, 1908; C. E. K. Mees and S. E. Sheppard, *Phot. Jour.*, 1910.

[2] *Phys. Rev.*, **10**, 234 (1900).

[3] *Physik. Zeit.*, **7**, 197 (1906).

[4] *Phys. Zeit.*, **5**, 5 (1904).

[5] See H. W. Fischer, *Ahren's Sammlung chem. tech. Vortr.*, **16** [4], 153 (1906).

declines, owing to the volatilization of one component, the cerium oxide. This is shown in the following table [1] :—

Time in hours . . .	0	100	200	300	400	500
HK horizontal . . .	103	108	105	98	95	93

Hence, for photo-chemical purposes, the mantle should not be used for more than 200 hours. It must hang in the hottest portion of the Bunsen flame, that is, the outermost, so the flame must be carefully adjusted and the mantle burnt in for some time. Further, the intensity depends, not only on the rate of supply of gas, but also on its admixture with air, as the following table from E. Saint Claire-Deville [2] shows :—

Gas.	Air.	Ratio $\frac{\text{air}}{\text{gas}}$	Light intensity absolute (Carcels).	Light intensity per 100*l* gas.
74·0	218·0	2·95	3·20	4·32
115·5	502·5	4·35	7·20	6·23
165·0	753·0	5·56	11·68	7·08
251·1	1155·0	4·60	17·31	6·89

The optimum value for the ratio of gas to air must therefore be determined by regulation of the air-supply.

Auer von Welsbach found, consequent on a series of researches on the emission spectra of the rare earths, that a mixture of thorium oxide, ThO_2, 99·1 per cent., and cerium oxide, CeO_2, 0·9 per cent., possessed by far the strongest emission for the visible rays, the intensity rapidly falling off for any other proportion. Various theories have been proposed in explanation of the superiority of this mixture in luminosity over the pure oxides. That "allactinic" radiation or "luminescence" was not in question was shown by the fact that the temperature of the Welsbach mantle is but little different from that of the Bunsen flame. Another theory supposed that the CeO_2 acted as a catalyzer for the combustion of the coal-gas, causing a much higher temperature in its neighbourhood, the thoria being simply the carrier for the catalyzer. It has

[1] *Schillings Kalendar*, 1906, p. 140.
[2] *Journ. f. Gasbel*, 1904, pp. 21, 46.

been shown, however, not only that the temperature difference is but slight, but also from researches of F. Haber[1] and F. Richard on the chemical equilibrium in the Bunsen flame, that the combustion takes place so rapidly that the loss of heat during the reaction is negligible. A thermal catalyzer could produce no effective rise of temperature, consequently the conception of any catalysis on the emission must be modified. The action is essentially photo-catalytic, and the formation of $CeO_2 . O_2$ is involved. The CeO_2 "activates" oxygen, and is regenerated by reduction of a peroxide. Further, it appears that the emission is quite independent of the process of combustion itself, since the same emission is obtained when the Auer mixture is heated electrically.

A physically adequate explanation has been found from consideration of the emission-curves of the pure oxides measured separately and when mixed.[2] Thorium oxide radiates feebly for the infra-red and the visible spectrum, consequently its loss by heat is slight and it takes up a very high temperature in the flame. On the other hand, ceria (CeO_2) in large quantities has a strong total radiation, and could not reach a very high temperature—it will be remembered that the higher the temperature of the radiating body, the greater the visible radiation. But dispersed in the thoria it takes the temperature of this, and gives practically "black" radiation in the visible spectrum, that is, the most intense possible for that temperature. Ruben's measurements showed that the Auer radiation is almost "black" for the blue region λ 470; the emission falls off rapidly in the near infra-red, again increasing in the extreme infra-red.

Whilst the particular emissive powers of ThO_2 and CeO_2 explain sufficiently well the increased luminosity obtained from the mixture, the problem remains as to why the maximum effect is dependent on a very narrow range of proportions of the oxides; why, in fact, some form of the "law of mixtures"

[1] Cf. *Journ. f. Gasbel*, 1904, p. 1143.

[2] A. le Chatelier and O. Boudouard, *C. R.* **126**, 1861 (1898); W. Nernst and E. Bose, *Phys. Zeit.*, **1**, 289 (1900); Ch. Fèry, *C. R.*, **134**, 977 (1902); H. Rubens, *Drude's Ann.*, **18**, 725 (1905); **20**, 593 (1906).

does not hold. In this conjunction the idea has been mooted[1] that the CeO_2 forms a solid solution in the ThO_2, and the 0·9 per cent. represents a saturated solution, any further quantity being only mechanically dispersed through the mass, and by its proper radiation in the red and infra-red, lowering the effective temperature. In fact, Rubens compares the action of the CeO_2 with that of a colour sensitizer in photography, which brings its own absorption strip into action in a desired part of the spectrum without affecting the remaining regions. And as we shall see later, similar quantitative relations hold in the case of colour sensitizers also.

The *mean temperature* of the Auer mantle, according to Rubens, is 1800° abs., or 1527° C. Relative values of its spectral intensity compared with sunlight and other sources are given later. The "light-effect" $\frac{\Lambda}{\Sigma}$ is given by Wedding as 0·010; the mean spherical intensity I as 52 HK. Modifications have been made in which gas and air are supplied under high pressure, by which much greater intensity is obtainable. The Lucas lamp, based on this principle, is said to give 1160 HK horizontal intensity.[2]

§ 40. Electric Glow-lamps.[3]

Filament lamps run off accumulators have frequently been used as constant light-sources, and as secondary standards. It is necessary to control the voltage carefully with a potentiometer, as the intensity varies rapidly with the electric potential. They must be burnt in first (about 10 hours), and worked a little below the normal pressure (reckoned for carbon filaments at 5 watts per 1 HK). Under normal current-load, the temperature of the filament is about 1600° to 1800° C., and the

[1] Cf. E. Baur, *Spektroskopie und Colorimetrie* (J. A. Barth, Leipzig, 1907), p. 23.

[2] See K. Schaum, *Photochem. u. Photograph.*, 1908, p. 178 (J. A. Barth, Leipzig).

[3] Cf. K. Schaum, *loc. cit.*, p. 180. On the photometry of electric lamps, see J. A. Fleming, *Electrician*, **50**, 438, 481 (1903).

surface brightness is 0·25 HK per sq. mm. In recent years lamps made with metallic filaments have been brought into use, such as the *osmium* lamp (due to A. von Welsbach), having a temperature about 1850° to 1910° C., and a surface brightness 0·3 HK up to 33 HK per sq. mm.; the *tantalum* lamp, the filaments of which, owing to its high conductivity, have to be very long and thin, has a temperature of about 1700° C. The life of these lamps is not very long, and they cannot be particularly recommended for photo-chemical work. The *osram* lamp has a filament of an alloy of osmium and tungsten. Recently lamps with filaments made from colloidal metals, prepared according to Bredig's method and then compressed, have been used.[1] J. T. Morris[2] has made a comparative survey of the different types of filament lamps.

Carbon filament lamps used as standards are best made with an extra-large bulb, as this does not darken so rapidly by the deposition of carbon. They should be of the high efficiency form, using $2\frac{1}{2}$ to 3 watts per c.p. Where it is desired to have as small a source as possible, the so-called *focus* lamps are convenient, in which the filament is coiled to a spiral or crumpled to a zigzag and brought to the focus of a concave mirror or a lens.

According to Fleming[3] the relation of the candle-power to the current is given by—

$$\text{C.P.} = aA^x$$

where A = amperes, a is a constant, and x a number between 5 and 6. Similarly for the voltage (see remark, p. 24)—

$$\text{C.P.} = cV^y \text{ nearly,}$$

where c is some other constant, and—

$$y = 6 \text{ nearly.}^4$$

The relation of the optical intensity of the *osmium* lamp to the Hefner standard has been measured throughout the

[1] *Zeit. f. Elektrochem.*, **4**, 514 (1898).
[2] *Electrician*, **58**, 318 (1906).
[3] *Encyc. Brit.*, 9th edit., Art. "Electric Lighting."
[4] See also Sir W. de W. Abney, *Photometry*, Cantor Lectures, Society of Arts, 1894.

spectrum by F. Leder,[1] and hence from the *known* values of the energies of the Hefner lamp throughout the spectrum (*vide* p. 81), the energy values of the *osmium* lamp were obtained (see Table VII.). From the curve of these plotted against wave-lengths, the value of the "black temperature" (p. 69) for any wave-length could be obtained, under the experimental conditions. Leder used a 25 HK lamp of the Auer Incandescent Lamp Co., for 40 volts, worked at 36 volts and 1·21 amperes, or a consumption of 43·56 watts.

TABLE VII.

Wave-length.	$K = \frac{\text{I Hefner}}{\text{I osmium}}$	$\text{E osmium} = \frac{\text{E Hefner}}{K}$
700 $\mu\mu$	0·4246	1266·6 ergs. secs.
680	0·3876	1154·8
660	0·3617	1011·0
640	0·3430	857·5
600	0·2963	605·2
550	0·2482	339·4
500	0·1996	167·1
480	0·1756	118·3
460	0·1571	80·7
450	0·1456	66·4
440	0·1343	54·1
430	0·1197	44·95

It must be remembered that these values are only accurate under Leder's experimental conditions.

The Nernst Lamp,[2] fed by the ordinary lighting current, cannot be used where great constancy is required, but is a convenient source of moderate intensities (60 to 250 HK horizontal). The filament, or rather rod, is composed of a solid solution of rare earth oxides, which form an electrolytic conductor for the current. This has to be previously heated to 600° C. before conduction takes place, which is accomplished by a side-shunt automatically put out of action when

[1] *Ann. d. Phys.* [4], **24**, 305 (1907). Leder used 25 and 36 HK lamps, which he found very constant on controlling the voltage.

[2] See W. Nernst and E. Bose, *Drude's Ann.*, **9**, 164 (1902); K. Schaum, *loc. cit.*, p. 183.

there is sufficient current passing. There is a "critical" value for the voltage, above which the filament is destroyed, to avoid which a special resistance is inserted, as, for example, iron wire sealed up in hydrogen, the resistance of which increases very rapidly with rise of temperature, hence with increasing current.

Intensity.—Lamps are delivered for—

	Model A.	Model B.	High power
Volts	96–250	96–250	220
Amperes	0·5	0·25–0·5	1
Intensities HK . . .	60–85	14–40, 28–46	250
Watts per HK . . .	1·48–1·51	1·85–1·66, 1·77–1·62	1·4

Size of Radiating Surface.—Rod, 0·04 to 1 mm. diameter, 10 to 30 mm. long.

Surface Brightness.—1 to 1·6 HK per sq. mm.

Temperature.—2100° C.

Useful Life.—400 to 500 hours.

For the relations of "loading" and intensity, etc., see reports by W. Wedding[1] and L. W. Hartmann.[2] Like other glow-lamps, the Nernst is a relatively poor source of violet and ultra-violet light.[3]

§ 41. The Arc Light.[4]

The arc discharge between carbon poles, affording a relatively intense source of small dimensions, and one rich in the rays usually most active in promoting photo-chemical change, has been very frequently used. The light differs in character and intensity in the different parts of the source;

[1] *Elektrotech. Zeitg.*, **22**, 620 (1901); **24**, 442 (1903).

[2] *Phys. Rev.*, **17**, 65 (1903).

[3] Cf. F. Sachs and S. Hilpert, *Chem. Ber.*, **37**, 425 (1904). They found a 1000 c.p. Nernst practically without effect on certain organic photo-reactions.

[4] Cf. K. Schaum, *loc. cit.*, p. 185; W. Biégon von Czudnochowski, *Das Elektrische Bogenlicht*, 1904; B. Monasch, *Der electrische Lichtbogen*, 1904; H. Ayrton, *The Electric Arc*, 1902.

the strongest emission is from the "crater" of the positive electrode; it is stated that in the ordinary arc the distribution is about as follows: positive crater, 85 per cent.; negative electrode, 10 per cent.; the arc itself, 5 per cent. The following table, by B. Monasch, shows the approximate intensities for ordinary arcs with continuous current :—

TABLE VIII.

Amperes.	Volts at lamp.	Diameters of carbons,		HK mean hemispherical.
		+ve	−ve	
6	39	14	9	400
8	40	16	10	620
10	42	18	12	850
12	43	20	13	1100
15	43·9	20	14	1450

The spatial distribution of the light,[1] due as it is to three separate radiators, is quite peculiar and has to be carefully considered when the arc is used for projection, photo-chemical investigations, etc. In Fig. 16 an approximate view of the way the ray bundles from the three portions are distributed is given. The maximum illumination occurs in the region A, all three sources being operative here; in b_1 the arc *plus* the crater are acting, in b_2 the arc *plus* the negative point, in c_1 only the crater, in c_2 only the negative pole. This is of course affected, *ceteris paribus*, by the inclination of the carbons to each other. Very convenient lamps are now made with the poles almost at right angles.

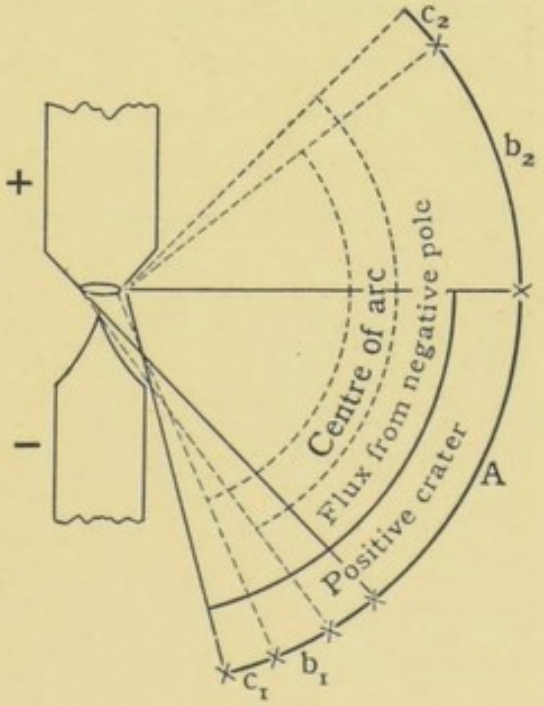


FIG. 16.

[1] See for calculations, photometry, etc., P. Högner; J. A. Fleming, *Elektrotech. Zeitg.*, **27**, 479, 686 (1906).

Constancy.—The possible causes of variation are so many that it is difficult to get even an approximately steady light from the arc. A very careful investigation by M. Wildermann,[1] of the conditions under which it may be used as a constant source for the investigation of photo-chemical dynamics, led to the following conclusions.

The low-current arcs of Körting and Mathiesen under ordinary conditions gave variations of 10 to 20 per cent. Where the "insolation" or exposure required was comparatively short the best results were obtained with a Dubosq form. The arrangement was that the current from accumulators passed through a Fleming variable resistance (3 ohms), the arc and the amperemeter.

A voltmeter could be connected either with the arc terminals or with the terminals of the accumulator-battery; provided the resistance in the circuit is kept constant, the higher voltage at the accumulator terminals compared to that at the arc terminals (67 volts compared to 42 volts in Wildermann's experiments) makes this arrangement more sensitive without loss of reliability. The light from the arc—in the direction of maximum illuminating power—fell symmetrically on the one hand on the photo-chemical reaction mixture or actinometer (in this case a photo-electric cell), on the other, and during the progress of the reaction, upon a Rubens thermopile connected with a Nalder galvanometer. The galvanometer deflections having been previously standardized, the radiant energy of the light could be expressed in absolute units. Under the best conditions for steadiness, the variations of the ammeter were rapid oscillations within 1 to 2 mm. for a total excursion of 31 mm., corresponding to 6·2 amperes, the volts being almost stationary. Continual slight oscillations about a mean may be reckoned as compensatory, the aim being to bring about the same auto-compensation as in making thermo-regulators. Wildermann recommends—

(*a*) The voltage at the terminals of the arc should be 42 volts, at the terminals of the accumulators 65 to 67 volts,

[1] *Phil. Trans. Roy. Soc.*, **206**, 335 (1906).

and the amperes in the circuit about 62 to 60. The standard resistance (3 ohms) should not be altered.

(*b*) The carbons must not burn down more than 1 to 2 cms., the incandescent surfaces should be kept as uniform as possible, the ends of the carbon poles being trimmed when necessary with a file. It was found that the short hard carbons of the London Electric Co. gave very good results, those used being 8 mm. in diameter for the upper, and 14 mm. in diameter for the lower pole; they were placed co-axially in a line making only a very slight inclination to the horizontal.

(*c*) There is a special distance between the poles—or spark-gap—which gives the most uniform illumination, and this must be determined by trial and error. Under these conditions a constant light over a limited period of time is obtained, when readjustment becomes necessary owing to the movement of the crater and the consumption of the carbons.

For an investigation of the photographic intensity of arc-light in the blue, green, and orange respectively, measured by the effects on panchromatic plates behind three-colour filters, see J. Precht and E. Stenger.[1]

§ 42. Light-sources for the Ultra-violet.

In many investigations it is desirable to have a source rich in ultra-violet radiation. As we shall see later, the increased photo-chemical activity of the shorter wave-lengths is no coincidence, but a connection of considerable theoretical importance. The quantitative measurements of ultra-violet radiation are rather scanty. Where the radiation is intense, A. Pflüger[2] has shown that absolute measurements with the thermopile can be made; it appears that the energy of the ultra-violet spectrum of the spark from metallic electrodes (Leyden jar discharge) is much greater than appeared from the photographic effect. Using an induction coil with Deprez's interruptor, the galvanometer throws are constant to 1 to 3

[1] *Zeit. wiss. Phot.*, **3**, 36 (1905).

[2] A. Pflüger, *Zeit. wiss. Phot.*, **2**, 31 (1904).

per cent. With aluminium electrodes the excursions, using a galvanometer of sensitiveness 1 div. per $4 \cdot 10^{-10}$ amperes, were approximately 200 to 300; the same values were obtained for the zinc lines at 203, 207, 210 $\mu\mu$, for the cadmium lines at 214, 219, 227, 231 $\mu\mu$, and for nickel, cobalt, and iron lines from 230–250 $\mu\mu$, and up to 900 div. for the magnesium lines at 280 $\mu\mu$. It is found that the maximum for the energy in the spark spectra of all these metals lies in the ultra-violet. Pflüger has applied the method to the determination of ultra-violet absorptions.

Spectro-photometric measurements in which a photographic plate replaced the eye, for use in the ultra-violet, were made by H. Simon[1]; the plate was drawn at a known rate before the ocular slit, and then the effective intensity determined by comparison with a plate having a known exposure. B. Glatzel made some modifications and measured the ultra-violet absorption of acetone and aqueous potassium nitrate, and later that of some aromatic hydrocarbons. Attempts have also been made to use an ocular of fluorescing material for quantitative work.

We may note that in high altitudes, the ultra-violet content of the sun's rays is far greater, owing to the lessened atmospheric absorption. Thus colourless glasses containing manganese are coloured violet in a few months at great heights—4000 metres—above sea-level, according to S. Avery, though even then the action is vastly slower than with a quartz-mercury lamp ($\frac{1}{2}$ – 12 hours).

Use has also been made of the photo-electric effect of the discharge of negative electricity from polished metals (*vide* Chap. VII.) by ultra-violet light. Elster and Geitel[4] have constructed a photo-electric photometer, which consists of a clean surface of rubidium in rarefied hydrogen. This surface is connected with the negative pole of a battery, whilst a

[1] *Wied. Ann.*, **59**, 91 (1896).

[2] *Phys. Zeit.*, **1**, 285 (1900); *Ibid.*, **2**, 172 (1900).

[3] P. V. Crookes, *Proc. Roy. Soc.*, 1905; S. Avery, *Brit. Journ. of Phot.*, 1905, 230.

[4] Eder's *Jahrbuch f. Phot.* (1895), p. 225.

platinum wire which passes through the spherical glass containing vessel connects with the positive pole; the indications of a sensitive galvanometer in the circuit are within wide limits proportional to the light-intensity. The radiation measured is that between 320 and 500 $\mu\mu$.

As a test for intense ultra-violet radiation C. Schall[1] recommends paper soaked in a solution of 1 gram of *p*-phenylene-diamine in 5 c.c. of dilute nitric acid (2 c.c. acid S.G. 1·2 to 3 c.c. water) dried rapidly in a Bunsen flame. The paper becomes blue on exposure to ultra-violet light. Rays from gas, Auer, electric glow, and Nernst lamps do not affect it.[2]

The arc between carbon poles is comparatively rich in these rays; still more effective is an arc with metallic electrodes, such as iron.[3] Most effective of all are the cadmium, and especially the mercury vapour arcs, *in vacuo*. Lamps on this principle are due to L. Arons[4] (1892), P. Cooper-Hewitt (1901), and others. Those for ordinary illumination, photographic purposes, etc., are of considerable length, 50 to 100 cms., but shorter forms are now constructed. The lamp is started by making a short circuit between the electrodes. The light is steady, even when the voltage varies considerably. In those constructed of glass the shorter ultra-violet is absorbed (beyond 300 $\mu\mu$), but Schott and Genossen Jena, supply a lamp made with "Uviol" glass transparent to 250 $\mu\mu$. They are from 20 to 130 cms. long, contain 50 to 150 grms. mercury, and the electrodes consist of platinum capped with carbon.[5] More convenient forms where it is desired to have a smaller source have been devised by H. Siedentopf, in which the light from a concentric electrode is used.[6]

The Heraeus mercury lamp, of fused quartz, offers the

[1] Eder's *Jahrb. of Phot.*, 1906, 39.

[2] *Phot. Work*, **33**, 321 (1907).

[3] Cf. E. C. C. Baly, *Spectroscopy*, p. 368.

[4] *Wied. Ann.*, **47**, 767 (1892), and **58**, 73 (1896). See also E. Hagan, *Journ. f. Gasbelg.*, **48**, 613 (1905).

[5] W. N. Hartley finds that the Uviol lamp lets little radiation beyond 328 $\mu\mu$ pass.

[6] See also the form designed by Barnes, *Astrophys. Journ.*, **19**, 190 (1904), and in Baly's *Spectroscopy*, p. 372.

most intense source of ultra-violet radiation available, fused quartz being transparent beyond 200 $\mu\mu$. In working with sources of ultra-violet rays, care should be taken to expose the skin as little as possible to the radiation, and in particular the eyes should be shielded with darkened glasses. Another source of ultra-violet is the spark-discharge; using a Leyden jar charged from an induction coil (10 cm. spark length), with cadmium electrodes an intense radiation at 275 $\mu\mu$, with magnesium electrodes, one at 280 $\mu\mu$ may be obtained.[1]

Mercury arc lamps suitable for chemical purposes, with a quartz jacket, are described by F. Fischer.[2] They are made with double-walled quartz cylinders fixed with sealing-wax into the neck of a surrounding cylindrical glass vessel connected with an air-pump. The anode consists of an iron ring, which surrounds the quartz cylinder and is suspended by means of two platinum wires fused into the glass vessel. Mercury placed at the bottom of the latter serves as the cathode. Arrangements are made to cool the lamp both internally and externally, so that the interior temperature is kept low, thus maintaining a low density of the mercury vapour and favouring the production of ultra-violet rays.

Sparks passed between aluminium terminals have been employed by W. H. Ross[3] as a source of ultra-violet light.

§ 43. Comparison of the Quality of Different Light-sources.

The *quality* of a light-source may be considered in two ways. Thermo-dynamically, it expresses the distribution of energy in its normal spectrum; relatively, the distribution of a particular photo-chemical intensity, the most important

[1] *Spectroscopy*, E. C. C. Baly, p. 373.

[2] *Ber.*, **38**, 2630 (1905).

[3] *Journ. Amer. Chem. Soc.*, **28**, 786 (1906).

[4] There is a weak ultra-violet emission from the flames of gas and acetylene, in the latter reaching beyond $\mu\mu$ 310. A. Amerio, *Atti R. Accad. Sci. Torino*, **42**, 673 (1907).

case of which is quality to the eye, the relative visual hue.[1] As we have seen, the absolute quality-value in the first case is best expressed by the constant $\frac{c_2}{T}$ of Wien's equation for the visible spectrum.[2] Spectrophotometric comparisons of the intensity-distribution can be used, as we have seen, to deduce the absolute quality, or thermo-dynamic distribution of energy, provided this is known from direct radio-metric determinations for one of them. But to give much of the data that has been obtained by comparison of different light-sources would serve no purpose, as even where the values are given in such a way that comparison is possible, it is evident, with few exceptions, that the quality of the light varies too much for the results of one set of experimental conditions to be accepted without redetermination as a basis of calculation for other investigations. Full references are given, however, since a rough idea of the quality of a light-source is frequently of value to workers in photo-chemistry and photography.

The spectrophotometric comparison of two light-sources may be expressed in two ways. In the first, the intensity for each wave-length of the one which is taken as normal is put equal to 1, and the values of

$$\text{the ratio } I'_\lambda / I_\lambda \text{ (normal)}$$

are obtained photometrically.[3] In the second, more frequently employed, the values of the ratios $\frac{I'_\lambda \text{ (source)}}{I_\lambda \text{ (normal)}}$ for different wave-lengths are divided by this ratio for one definite wave-length λ_o, which is equivalent to equating the intensities of the two lamps for λ_o; this can of course be arranged for experimentally, by cutting down the intensity of one of the lights by any method which does not affect its quality (*vide* p. 26). By plotting the values of these quotients—

$$\frac{I'_\lambda \text{ (source)}}{I_\lambda \text{ (normal)}} \Big/ \frac{I'_{\lambda o} \text{ (source)}}{I_{\lambda o} \text{ (normal)}}$$

[1] Of course, the second case depends upon the first.

[2] Not for discontinuous spectra.

[3] A. Rudolphi, *Z. f. Gasbel.*, 1905, 217.

as ordinates against wave-lengths as abscissæ, we obtain characteristic curves of the light-sources, all cutting the line of the normal lamp, which runs parallel to the abscissæ at an ordinate 1, at the point corresponding to λ_o. Such curves are given by Hartmann,[1] acetylene burning in air being taken as normal. See Fig. 17.

Measurements of this type have been made by H. C. Vogel[2] ($\lambda_o = 555\ \mu\mu$) for the sun, arc, skylight and moonlight, with a petroleum lamp as normal; by Hartmann for the lamps given in figure, by W. Nernst and E. Bose[3] for glow-lamps, Welsbach and arc light (glow-lamp as normal), and by Else Köttgen[4] for a large variety of light-sources, the Hefner lamp being taken as normal and $\lambda_o = 590\ \mu$. The measurements may be classified into four sets: (*a*) petroleum and solar oil burners; (*b*) gas-burners; (*c*) incandescent Welsbach-light; (*d*) sun and sky. They were made with a König spectrophotometer, and are among the most valuable up to the present; but for modern purposes a series of such comparisons using electric sources is required.

Less exact, but of considerable value for orienting purposes, are similar measurements not made spectrophotometrically, but in which different spectral regions are cut out by filters and compared for different pairs of lamps, just as was done in the foregoing investigations for practically monochromatic spectral regions.[5] For measurements of a large number of modern sources made in this way, see W. Voege.[6]

The preponderance of blue and green in the Welsbach light compared with ordinary gas is very evident. There is a considerable difference in the quality of the Welsbach light for

[1] L. W. Hartmann, *Phys. Zeit.*, **5**, 5 (1904).

[2] H. C. Vogel, *Berl. Ber.*, 1880, 801.

[3] *Phys. Zeit.*, **1**, 290 (1900).

[4] *Wied. Ann.*, **43**, 793 (1894).

[5] The difference in method is comparable to that between determining the sensitiveness wave-length curve of a photographic plate, and its relative sensitiveness quotient behind selected filters. See *Theory of Phot. Process* (Longmans, 1906), p. 279.

[6] *Journ. f. Gasbel*, 1905, 512; K. Schaum, *Photochemie*, p. 195.

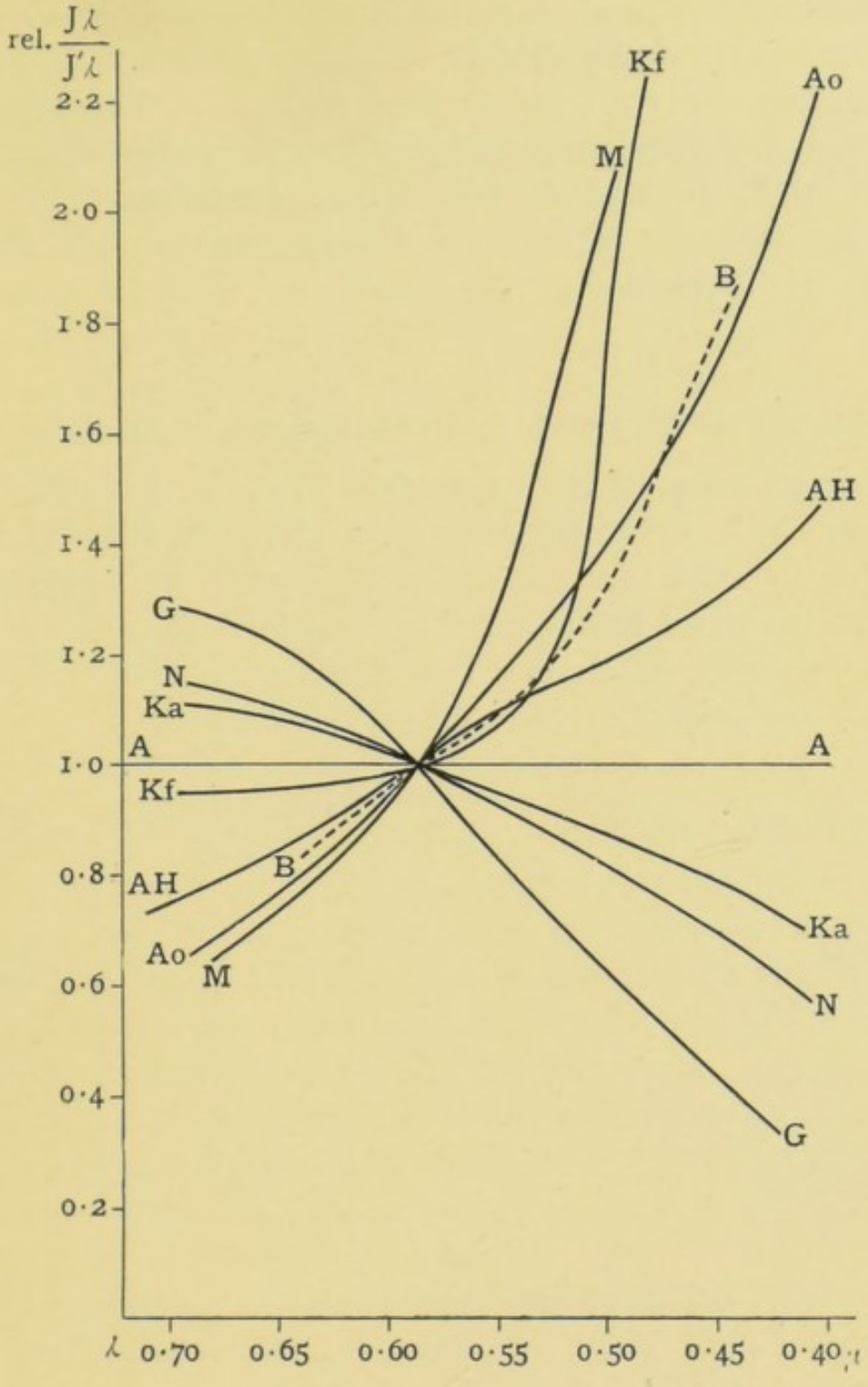


FIG. 17.

A = Acetylene flame in air.
Ka = Limelight (old lime).
N = Nernst lamp.
G = Ordinary gas-flame.
Kf = Limelight (fresh lime).
AH = Acetylene-hydrogen flame in oxygen.
Ao = Acetylene flame in oxygen.
B = Electric arc.
M = Magnesium light

different mantles, and it varies in the first days of use, then reaches a fairly steady value.

Measurements for 10 spectral regions of limelight, arc, sun, and daylight, compared with a 16 c.p. glow-lamp, were made by E. L. Nichols and W. S. Franklin.[1] For other measurements of a similar type, less recent, see O. E. Meyer[2] and W. H. Pickering.[3]

§ 44. Photochemical Comparison of Light-sources.

The meaning of the expression "relative actinism" of a light-source is explained later (p. 115). The following table is given by Eder[4] for the chemical intensity of certain light-sources for silver bromide on development, the Hefner lamp being taken as standard. The values only serve to indicate roughly the proportion of violet and ultra-violet.

Light-source at 1 metre.	Relative optical intensity in HK.	Chemical intensity, H.M.S.	Relative actinism.
Hefner	1	1	1
Limelight	70	260	3·7
Argand	16	28	1·75
Auer or Welsbach	60	160	2·6
Arc	400	4000	10·0
Mg ribbon per 1 *mg.* in air	135	435	23·8
Mg through colourless glass	—	270–400	—
Mg through colourless glass in oxygen per 1 *mg.*	—	769	—

Actually, the most important energetic data for what may be termed pure photo-chemistry are the values of the total energy radiated and the spectral distribution of the energy. Unfortunately, the principal direct determinations, by the bolometer or otherwise, for ordinary light-sources, lie outside

[1] *Amer. Journ.*, [3] **38**, 100 (1889).

[2] *Zeit. f. angew. Elek. Lehr.*, **1**, 320 (1879).

[3] *Proc. Amer. Acad.*, **15**, 236 (1880).

[4] J. M. Eder, *Sitz. Ber. Wien. Akad.*, 1903, April; *Beitr. z. Photochemie*, II. 149.

the regions of the spectrum which are mainly considered in promoting chemical change, viz. the visible and the ultra-violet regions.

Suppose the curve in Fig. 18 be the energy curve (*i.e.* the energy *modulus* curve) of a light-source, and suppose the region affecting a certain photo-chemical reaction be that comprised between $\lambda_1 - \lambda_2$. Now it is evident that in evaluating the influence of the wave-length of the light upon the reaction, that we cannot say that that light of wave-length λ_n has greater influence on the reaction than that of λ_m, or that the maximum lies at λ_p, unless the relative intensities of these have been made equal. Let us consider the question more fully. One characteristic (*vide* p. 106) of a photo-chemical reaction is spectral sensitiveness. The "sensitiveness" is necessarily a quantity difficult to define; we may for the present consider it as a velocity-constant, or as the proportion of a reacting substance changed in unit time.[1] It is required to know the relation of this to the wave-length of light acting. We assume the possibility of making measurements at sufficient spectrum intervals of approximately monochromatic character. The quantity taken as a measure of the light-action is then plotted against the wave-length of the light, and this gives the spectrum sensitiveness.

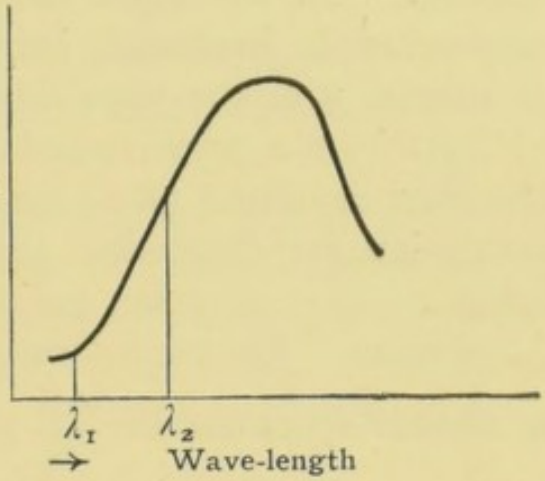


FIG. 18.

§ 45. CHOICE OF CO-ORDINATES.

But it is necessary, if results of comparative value are to be obtained, to choose the co-ordinates properly. The

[1] Practically, in many photochemical reactions, we take the time necessary to produce a given (constant) quotient of change. The reciprocal of this may be considered as proportional to the reaction velocity (W. Ostwald, *Lehrbuch d. allg. Chemie*, 2nd edit., **2**, 236).

abscissæ, wave-lengths, must be based on a normal spectrum, *i.e.* one in which the distances between spectral lines are proportional to the differences of their wave-lengths. Such a spectrum is furnished by a grating, either flat or concave, so long as the surface receiving the spectrum is normal to the grating.[1] On the other hand, in all prismatic spectra, the dispersion is irrational, being compressed at the red end compared with the ultra-violet. In addition the absorption of light by the prism material causes a further departure from the ideal condition of an iso-energetic spectrum. Hence, the correction for dispersion alone does not yield satisfactory results. This may be accomplished by a method due to L. Mouton.[2] Let the indicating effect produced by the rays of a normal spectrum be $\frac{\Delta S}{S}$ for the small spectrum interval $\lambda_1 - \lambda_2 = \frac{\Delta\lambda}{\lambda}$; this "effect" we need only consider at present as the parameter of a generalized co-ordinate; it may be the galvanometer throw of a bolometer, hence a measure of energy as heat, which can by reduction by expressed in absolute units, or it may be the "density" of a photographic image, that is, an approximate measure of a photochemical reaction. But in any case, the effect is to be taken as a function of an activity *sui generis* proper to a mean wave-length of definite position in a normal spectrum. Now, in a prismatic spectrum, the effective energy per infinitesimal interval $d\lambda$ depends upon the angular dispersion, being very nearly inversely proportional to this. Suppose that the value of the uncorrected effect $\frac{\Delta S}{S} = y$ at a value δ of the angular deviation, and that the value of the corrected effect be $x\lambda_\mu$, then—

$$x = y\frac{\Delta\delta}{\Delta\lambda}$$

when δ is the angular deviation. The correction is best carried out graphically in a manner due to S. P. Langley.[3]

[1] See E. C. C. Baly, *Spectroscopy*, p. 38.

[2] *C. R.*, **89**, 295 (1879); also H. Kayser, *Hdbuch d. Spektros.*, I. 751.

[3] Cf. H. Kayser, *Hdbuch d. Spektros.*, **1**, 751.

Angular deviations of the spectrometer scale are plotted as ordinates, corresponding wave-lengths of well-known spectrum lines as abscissæ, which gives a dispersion curve. At values of δ for which the "effect" (thermal action or photochemical effect) has been measured, the value of $\frac{d\delta}{d\lambda} = \tan \phi$ is read off; the corresponding value of the "effect" multiplied by this gives the corrected "effect" for a mean wave-length in a normal spectrum.

But this correction alone does not give a faithful return of the influence *the particular distribution of energy* of the source in question has on the phenomenon measured, since no allowance is made for the absorption of light by the prism. The effect of this is shown in the two figures due to R. J. Wallace.[1] The first (Fig. 19A) represents the prismatic spectrum ($\mu_D = 1{\cdot}6994$) taken on a photographic plate and the densities plotted. A wave-length scale (dispersion-curve) being then prepared, the density and wave-length curve was reduced as described above, the results of which are shown in Fig. 19B (*a*). On the same scale are plotted the results obtained with a replica-grating upon a similar plate, the value of whose region of highest density was practically identical with that of the reconstructed curve of the prismatic spectrum (see Fig. 19B (*b*)). It will be seen that there is a marked lack of agreement, not only a deficiency in the ultra-violet, but a shifting of the maximum of sensitiveness to the red. Wallace states that he hopes to obtain a formula taking account of the loss due to absorption by the prism. In the mean time he points out that even in diffraction spectra, abnormalities of distribution occur, especially with gratings ruled on speculum metal, which possesses a selective absorption varying with the different specimens. Further, in direct ruled gratings, the distribution of energy varies with the nature of the groove made in cutting, so that no two gratings give the same distribution. He suggests as a standard dispersion-piece in sensitometry replicas made

[1] R. J. Wallace, *Astrophysical Journ.*, 1908; *Brit. Journ. of Phot.*, 54, 369 (1908).

in collodion, under standard conditions, from the same original.[1]

So much for the dispersion piece and its influence. Assuming that reduction to normal dispersion has been satisfactorily accomplished, we will return to the distribution

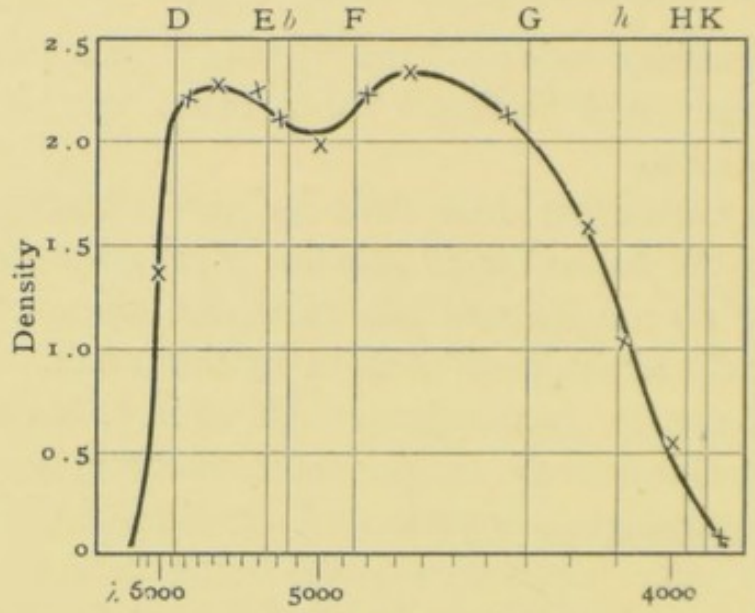


FIG. 19A.

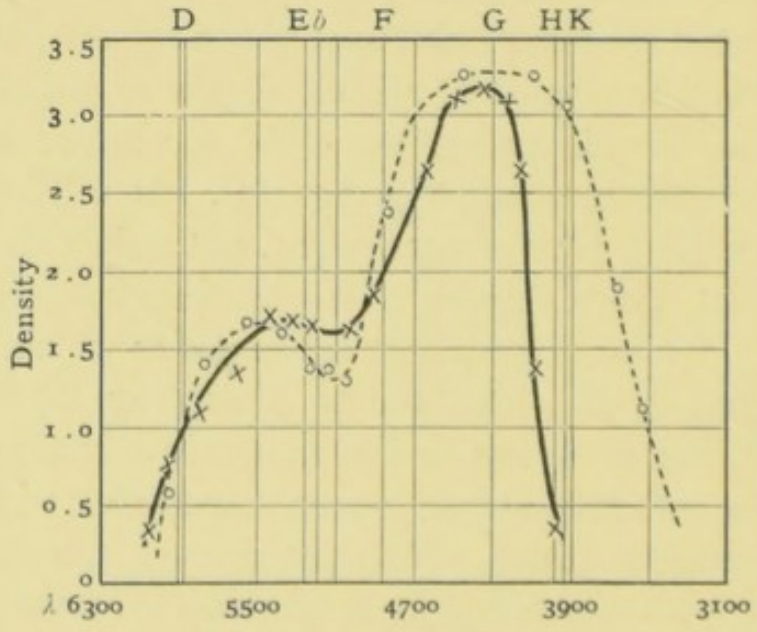


FIG. 19B. ——— = (*a*)
..... = (*b*)

of energy in light-sources themselves, and the choice of co-ordinates in representing the influence of the wave-length on chemical reactions. The best way would be undoubtedly

[1] For details, see *Astrophys. Journ.*, **22**, 129 (1905).

the direct determination, by means of a line-bolometer, radiomicrometer or other radiometer, of the energy curve over the given spectral region under the same conditions as those for the photochemical reaction. Dividing the "sensitiveness" values by the corresponding values of the energy for the same wave-lengths,[1] we obtain a representation of the effect of a spectrum of equal energy. A better method of representation is to choose the *logarithms* of the "sensitiveness" as ordinates,[2] when the correction for energy distribution is obtained by simple subtraction of the logarithm of the energy for a given wave-length from the logarithm of the sensitiveness.

§ 46. Calculation of the Energy Curves.

The energy curves for certain light-sources have been measured, in other cases spectrophotometric comparisons in the visible spectrum have been made (*vide* p. 100), and the energy curves can be calculated by using Wien's equation, for the region in which photochemical activity is most evident, provided that the source can be considered as a "black body."

The validity will depend on the temperature of the radiator.[3] We cannot, for example, apply Wien's equation to the sun, but for sources the temperatures of which lie below 3000° abs. the Wien law is applicable up to wave-length 10,000 $\mu\mu$. E. Hertzsprung[4] has calculated the values of log S_λ (the relative energy intensities) of the black body for different temperatures, as also the optical intensities for the normal grating spectrum, using Planck's equation.

The values for the optical intensities were obtained as follows. From numerous determinations[5] of the spectral

[1] This assumes a certain relation, namely, that the photochemical effect is proportional to the light intensity.

[2] E. Hertzsprung, *Zeit. wiss. Phot.*, **3**, 18 (1905). He points out that by keeping to logarithmic quantities the *desired* ordinates are obtainable chiefly by additive processes.

[3] See p. 65.

[4] *Zeit. wiss. Phot.*, **4**, 43 (1906).

[5] The "sensitiveness" is the first perceptible difference of intensity; it depends both on the total intensity and on the wave-length. The values

sensitiveness of the eye, Hertzsprung calculates as the most probable values for the logarithms of this, log H_λ

λ in $\mu\mu$	0·75	0·70	0·65	0·60	0·55	0·50	0·45	0·40
log H_λ	−4·04	−2·19	−0·97	−0·20	0·00	−0·47	−1·08	−1·36

then $$\text{rel. log } I_\lambda = \log H_\lambda + \text{rel. log } S_\lambda$$

and $$\Sigma = \int_0^\infty I_\lambda d\lambda = \int_0^\infty H_\lambda S_\lambda d\lambda$$

The total intensities, given by the above integral, Hertzsprung obtained by planimetric measurement of the curves of the I_λ values, and these give the values of the (total) surface brightness of the black body for different temperatures, with which, however, we are not further concerned, their importance being chiefly for optical pyrometry.[1]

The Sun and Daylight.—The light of the sun, whether in its direct form or as diffused daylight, is the most available and immediate source and naturally is the normal to which, in regard to colour, artificial light-sources must approximate.

Many investigations have been made of the rate at which the sun radiates heat. The "solar constant," as it is termed, is the total radiation per minute falling perpendicularly on 1 sq. cm. at the earth's mean distance. It is necessary to distinguish, however, between the values outside the earth's atmosphere and that actually incident on the earth's surface after undergoing absorption. The former is termed the "extra-terrestrial" radiation, the latter, "terrestrial"; we may distinguish the corresponding values of the solar constant by R_e and R_t.

The values obtained vary considerably.[2] The most reliable

are for an iso-energetic spectrum, calculated by Hertzsprung (*loc. cit.*) from the observations of A. König (*Beitr. z. Psychologie u. Physiologie d. Sinnesorgane*, Hamburg, 1891; A. Pflüger, *Drude's Ann.*, **9**, 185 (1902); S. Langley, *Amer. Jour.*, (3) **36**, 359 (1888); W. de W. Abney, *Proc. Roy. Soc.*, **49**, 509 (1891). On the whole subject see K. Schaum, *Photochem u. Photophys.*, p. 70, v. 1 (A. Barth, Leipzig, 1908).

[1] See E. Hertzsprung, *loc. cit.*, and K. Schaum, *Photochem. u. Photophys.*, VI. p. 162.

[2] See J. Scheiner, *Strahlung u. Temperatur d. Sonne*, 1889, p. 32.

determinations are probably those of S. P. Langley,[1] who gives for R_e 2·63 – 3·50 gram-calories.

To obtain the value of R_e from the actually recorded measurements of R_θ, it is necessary to correct for the absorption by the atmosphere, which is accomplished by determining R_θ for different altitudes of the sun. The method of Langley[2] consists in measuring with the spectrobolometer the energy curve for a high and a low altitude of the sun; the difference, taking account of the thickness of the atmosphere traversed, enables us to determine the extinction-coefficient for the different wave-lengths and thus construct the energy curve of the extra-atmospheric radiation. The planimetry of this gives the value of R_e. Langley gives[3] 25 values determined for this, the mean being ca. 2·1 $\frac{\text{gram-cal.}}{\text{cm.}^2 \text{ min.}}$

This would correspond to the radiation of a "black body" at a temperature of 5990° abs. The latest researches of Abbot[4] give from the energy distribution in the extra-atmospheric spectrum a temperature of 6356° abs. The value of R_e can be expressed, from the Stefan-Bolzmann law, by the following formula:—[5]

$$R_e = 60\, S_{abs.}\, c_2^4 \left[\frac{T}{C_2}\right]^4 \sin^2 \psi$$

where $S_{abs.}$ is the radiation constant (p. 73), ψ the angular radius of the sun, and $\frac{c_2}{T}$ is the "quality constant" in Wien's equation.

Knowing the value of $\frac{c_2}{T}$, we can calculate R_e from this, or conversely. From Abbot's determination E. Hertzsprung has calculated the value of $\frac{c_2}{T}$ for Planck's equation, which

[1] *Phil. Mag.*, [6] **8**, 78 (1904).
[2] *Wied. Ann.*, **19**, 226, 384 (1883).
[3] *Phil. Mag.*, *loc. cit.*, p. 80.
[4] C. G. Abbott, *Smithsonian Miscellaneous Contributions*, **45**, 74 (1903).
[5] F. Kurlbaum, *Wied. Ann.*, **65**, 746 (1898).
[6] *Zeit. wiss. Phot.*, **3**, 173 (1905).

gives the best correspondence with the observed energy distribution; he finds $\frac{c_2}{T} = 2{\cdot}3$, then from the above—

$$R_e = 60 \times 1{\cdot}277 \times 10^{-12} \left[\frac{14580}{2{\cdot}3}\right]^4 \sin^2\psi$$

$$= 2{\cdot}64 \frac{\text{gram-cal.}}{\text{cm.}^2 \text{ min.}}$$

§ 47. Distribution of Energy in the Solar Spectrum.

Hertzsprung concludes that the radiation of the sun outside the earth's atmosphere corresponds, with fair approximation, both qualitatively and quantitatively, to that of a black body having for $\frac{c_2}{T}$ the value 2·3 to 2·4. If we take as a mean value for $R_e = 2{\cdot}50 \frac{\text{gram-cals.}}{\text{cm.}^2 \text{ min.}}$, we obtain, for the rough division of the energy into infra-red, and visible radiation from Langley's measurements—

	Total.	Infra-red.	Visible (+ ultra-violet).
R_e	2·50	1·37	1·13
R_t	1·60	1·00	0·60

The principal investigations of the energy distribution of the solar radiation are due to Langley[1] and his co-worker Abbot. By means of the "spectrobolograph" he could obtain within 15 minutes a complete record of the distribution of energy in the sun's spectrum, photographically recorded, from the violet to 6μ. The means of Langley's earlier observations are given in the table.

[1] *Loc. cit.* and *Astrophys. Journ.*, **17**, 89 (1903). For an account of the experimental methods, see E. C. C. Baly, *Spectroscopy*, pp. 226 *et seq.*

Addendum.—The most recent and complete discussion of the "solar constant" and the absorption of the atmosphere for solar radiation will be found in the *Annals of Astrophys. Lab. of Smithsonian Ins.*, **2**, pp. 1–237 (1908); it deals with the work of the observatory from 1900–1907; the most probable value of R_e is 2·1 $\frac{\text{gm.-cals.}}{\text{cm.}^2 \text{ min.}}$ which, however, varies, both from solar and terrestrial changes. A layer of water vapour at 4000–5000 ft. "lags" the earth's heat.

TABLE IX.

$\lambda(\mu)$.	S_λ extra-terrestrial.	S_λ terrestrial.	
		a	*b*
0·375	3·53	112	27
0·400	683	235	63
0·450	1031	424	140
0·500	1203	570	225
0·600	1083	621	311
0·700	849	553	324
0·800	519	372	246
0·900	316	238	167
1·000	309	235	167
	λmax 0·52	λmax 0·59	λmax 0·67

The values of S_λ given are the galvanometer excursions. Column *b* gives the results for a lower altitude of the sun than for column *a*, such that the thickness of the atmosphere traversed would be twice that for *a*. It will be seen that the relative distribution and the position of the maximum depend very considerably on the thickness of atmosphere traversed. The fact is of great importance for the photo-chemical measurement, or "actinometry" of the sun's radiation, and does not appear to have been sufficiently considered. This "quality" value, as it may be termed, of a light-source, may be expressed, so long so it can be considered as a black body, by the constant $\frac{c_2}{T}$ of the radiation-function (see p. 64). Hertzsprung[1] has calculated from Langley's measurements, the change which the value $\frac{c_2}{T}$ for the visible

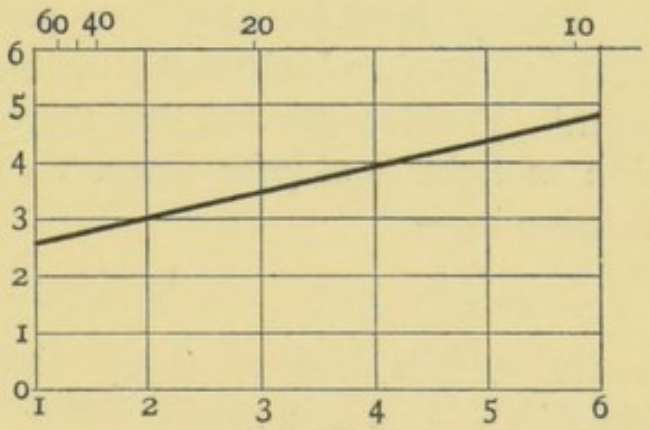


FIG. 20.

[1] E. Hertzsprung, *Zeit. wiss. Phot.*, 1907.

spectrum (0·4 to 0·7 μ) undergoes in passing through one atmosphere, which he finds to be 0·4 ± 0·1, where ± 0·1 is the deviation of the observation on any day from the mean. In the curve is shown an approximate representation of the change in the value of $\frac{c_2}{T}$ with the sun's height for clear days (Fig. 20).

Abscissæ.—Cosecants of the sun's altitude = sec ϕ (*vide* p. 111).

Ordinates. — $\frac{c_2}{T}$ values for the visible solar spectrum.

From this we may reckon that the winter sun in our latitude has a value for $\frac{c_2}{T} = 4$, which would correspond roughly with burning magnesium. The total daylight, however, is of course modified in quality by the skylight, and is therefore bluer, especially at low altitudes of the sun.

§ 48. Absorption of Light by the Atmosphere.

Various formulæ have been proposed to express the effect of the atmosphere's absorption upon the intensity of direct sunlight.[1] Pouillet assumed that the ordinary law for the absorption of light held (*vide* Chap. V., p. 143), and expressed the relation by—

$$I_t = I_o p^{-m}$$

where I_o is a constant (proportional to the extra-terrestrial intensity), p is a constant called the absorption-coefficient, and m is the mass of atmosphere traversed. Crova and Bartoli proposed modifications, which, however, are not much to be preferred to that of Pouillet, since they also do not hold over the whole range of observation. Pouillet's relation may be written—

$$\log_r I = a_1 - b_1 m$$

where a_1 and b_1 are constants, whilst m is evidently some

[1] Cf. A. Bemporad, *Meteorol. Zeit.*, 1907, p. 306.

function of the sun's zenith-distance (90° − altitude) ϕ [1]. Neglecting the earth's curvature (see Fig. 21),

let cb = direction of zenith
ca = direction of sun
$a\hat{c}b = \phi$

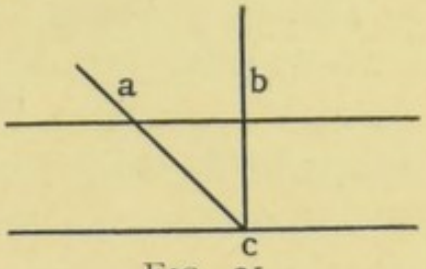


FIG. 21.

it is obvious from the figure that—

$$m = F(\phi) = h \sec \phi = h/\cos \phi$$

where h is a constant, proportional to the perpendicular thickness of the atmosphere, and hence to the height of the barometer. We can therefore write for Pouillet's formula—

$$I_t = I_o p^{-\frac{P}{760 \cos \phi}}$$

or

$$I_t = I_o \, 10^{-\frac{aP}{760 \cos \phi}}$$

where a is the thickness of atmosphere traversed which reduces the original intensity $\frac{1}{10}$. This was the formula used by Bunsen and Roscoe in their actinometric researches (*vide* p. 117). At low altitudes of the sun we cannot, however, neglect the earth's curvature, for it is obvious since $m \propto \sec \phi$, that the value of m would then approach ∞. It has been proposed to use Lambert's construction.

$$m = \frac{1}{h} \sqrt{h^2 + 2rh + r^2 \cos^2 \phi} - r \cos \phi$$

where r = earth's radius, h = height of earth's atmosphere, assumed homogeneous. However, it is not homogeneous, and a better expression is that used by Laplace [3] for the relative thickness; according to this the *relative thickness* $m = \frac{n}{K \cdot \sin \phi}$, where n is the astronomical refraction corresponding to ϕ.

[1] The zenith-distance may be obtained by direct measurement of the altitude, or when this is not feasible, from the equation $\cos \phi = \cos \delta \cos t \cos p + \sin \delta \sin p$, where δ is the sun's declination on the day of observation, p = the latitude, and t is the solar time in degrees. For the influence of the zenith-distance on radiation, see also Sv. Arrhenius, *Lehrb. d. Kosmischen Physik.* (S. Hirtzel, Jena, 1903).

[2] Lambert, *Photometria*, Ostwald's *Klassiker*, Nos. 31, 32 (Leipzig).

[3] Cf. A. Londe, *L'Actinométrie*, p. 129.

This is itself a function of the atmospheric temperature gradient.

Instead of Pouillet's expression, which in logarithmic form is, as we have seen,

$$\log I_t = a_1 - b_1 m,$$

Bemporad finds the parabolic form

$$\log I_t = a_2 - b_2 m^l,$$

where l = a proper fraction, to be satisfactory over the whole variation of ϕ, but m is obtained by rigid use of Laplace's function, assuming a definite temperature-fall through the atmosphere. Bemporad has calculated tables of the values m^l for different values of ϕ, by which the application of the more complex form becomes much simplified.

For altitudes greater than 10°, the expression of Pouillet, with m taken as proportional to sec ϕ is fairly satisfactory. Strictly speaking, in the expression $I = I_0 10^{-\frac{\alpha P}{760 \cos \phi}}$ the values of α, the extinction coefficient can be different for each wave-length, so that if the original intensities be I_1, I_2, etc., the intensity after transmission will be—

$$I' = I_1 10^{-\alpha_1 m} + I_2 10^{-\alpha_2 m} + \text{etc.}$$
$$= \Sigma 10^{-\alpha_\lambda m}$$

The value of I′ can then only be obtained by using a dispersion-equation or interpolation formula, expressing the complex conjugation between α the extinction, and λ the wave-length; but, as will be seen, the expression is generally used in actinometry as true for a considerable breadth of the spectrum.

§ 49. The Actinometry of Sunlight.

Actinometry has been sometimes used as a general term for the measurement of solar radiation, but it is generally restricted to the measurement of the intensity of radiation by chemical means. The general methods and laws will be dealt with in another chapter; we shall confine ourselves here to the determination of the chemical intensity of sunlight. It must be clearly understood that there is, however, no absolute value

in this term. For as light of every wave-length is capable of affecting some *one* particular chemical reaction, and since, as we have just seen, the solar spectrum is composed of rays of all periods of vibration, we could theoretically measure by suitable choice the chemical intensity of any group. Further, the energy varies from wave-length to wave-length, and the ratio of the energies changes according to the nature and thickness of the atmosphere traversed, consequently different actinometers selecting different portions of the sun's spectrum will not give comparable results. *The data of any particular actinometer are only of individual value.* Only when effected by the same region of the spectrum, that is, when they have the same curve of sensitiveness (*vide* p. 106), are the indications of two actinometers comparable. What has been said here concerning the sun's radiation applies with equal force to every other light-source. It is often loosely stated that one light is more *actinic* than another. By this is usually meant that it is richer in the shorter wave-lengths—violet and ultra-violet—since the majority of photo-chemical reactions are due to these. The *relative actinism* of two light-sources depends upon the chemical reaction used to compare them. The *relative actinism*, for a given reaction, is the ratio of the chemical intensities, divided by the ratio of the optical intensities. For example, Eder found that[1] 1 *mg.* of magnesium burnt in a ribbon had the same effect per second on a silver bromide plate as an exposure of 435 seconds to a Hefner lamp at 1 metre. Hence the chemical intensity of 1 *mg.* magnesium for silver bromide = 435 HK.M.S. For silver chloride, the chemical intensity per 1 *mg.* Mg was similarly 872 HK.M.S. Now, the optical intensity of Mg burnt at 7·4 *mg.* per second, was found to be 135 HK. Hence the *relative actinism* of magnesium for silver bromide

$$= \frac{7{\cdot}4 \times 435}{135} = 23{\cdot}8$$

and for silver chloride $\dfrac{7{\cdot}4 \times 872}{135} = 47{\cdot}8$

[1] J. M. Eder, *Beiträge zur Photochemie*, Part II., p. 149

Thus, keeping to the same standard light-source, say the Hefner, and the same photo-chemical effect, say that of the silver bromide plate, we could obtain in this way a comparison of the so-called actinic powers of different light-sources.

It has been repeatedly shown that the ordinary optical laws hold for the rays acting chemically. Beside these, there is one prime condition upon which actinometry as a quantitative science depends. That is the so-called *reciprocity law*. A photo-chemical change will be in general greater the greater the intensity of light. If we denote by $A \rightarrow B$ the change, then the photo-chemical effect will be measured by a definite quantity of B produced from A. This effect, which may be termed E, should always correspond to the same amount of light-energy. The total amount of light or "light-flux" (*vide* p. 77) over a time t will be equal to It, where I is the intensity. Then the photo-chemical effect E should be proportional to this, *i.e.* $E = k \cdot It$. This is the so-called "reciprocity" law, which states that the same photo-chemical effect is obtained with a light-sensitive reaction for the same amount of light, whether the intensity be diminished and the time proportionately increased or conversely. The product It is sometimes termed the "insolation" (Bunsen and Roscoe), or the exposure, and the practical photographer relies upon the validity of the reciprocity law every time for determining the correct exposure. It has been found valid within certain limits for the chlorine-hydrogen actinometer[1] for the darkening of silver chloride,[2] or generally for photographic processes with silver salts, for the decomposition of ferric oxalate,[3] and certain other reactions. We shall return to the question later in dealing with the general theory of photo-chemical change; we may consider it established for the actinometric measurements of sunlight now described, so that the photo-chemical effects measured could be regarded as trustworthy indicators of the amounts of light involved.

[1] *Phil. Mag.*, [3] **23**, 466 (1873), J. W. Draper.

[2] R. Bunsen and H. Roscoe, *Pogg. Ann.*, **117**, 536 (1862).

[3] Marchand, *Étude sur la force chimique contenue dans la lumière du soleil*, 1875.

§ 50. The Practical Value of Actinometric Researches.

Although the very sensitive bolograph of Langley will record vibrations well into the early ultra-violet, yet it is upon the chemical reactions of the photographic plate that we depend chiefly for cosmic photometry. Actinometric research is of importance, *inter alia*—

(*a*) For meteorology and cosmic physics, in determining the effect of the atmosphere on certain groups of spectral rays, from which again conclusions both as to the variation of the atmosphere, and the best conditions of time and place for astronomical photography may be drawn.

(*b*) For bio-geography, since the photo-chemical climate is an important factor regulating the distribution of plant, and hence also of animal life upon the globe.[1] Under this we may also include its value for agricultural science.

(*c*) For the general practice of photography. The researches of Bunsen and Roscoe and others have furnished the material for the exposure tables and guides familiar to most photographers.

The first actinometric measurements of sunlight were made by Saussure,[2] the pioneer of alpine exploration. He made use of Berthollet's discovery of the decomposing effect of light on chlorine water to construct an actinometer, and also employed papers coloured with vegetable tinctures (1790). Although different types of actinometers were constructed (see Chap. I.), no further investigation of a general character was made till Bunsen and Roscoe commenced their epoch-making "Photo-chemical Investigations" (1854). They may be said to have founded actinometry as a quantitative science, and we shall deal with their researches in some detail.

[1] Cf. Bunsen and Roscoe, *Pogg. Ann.*, **108**, 193 (1859).

[2] H. B. de Saussure, "Effets chimiques de la lumière sur une haute montagne comparés avec ceux qu'on observe dans les plaines," *Mémoires de l'Acadamie de Turin*, IV., 441 (1790); and Crell's *Chem. Ann.*, I. 356 (1796).

§ 51. The Chemical Intensity of Direct Sunlight.

We have seen that the intensity of light is altered by traversing the atmosphere in a manner expressed by the equation—

$$I = I_o \, 10^{-\frac{aP}{\cos \phi}}$$

Bunsen and Roscoe, assuming that all the rays acting on the mixture of hydrogen and chlorine in their actinometer (*vide* p. 241) had the same value of a, compared the deductions from this formula with the observed workings of the actinometer for different altitudes of the sun. The agreement (see Table X.) is fairly good, considering the difficulty of the experiments and the many calculations necessary for the deduction of the photo-chemical effect; this agreement we might put down to the fact that the rays chiefly acting form a narrow portion of the

Table X.

Zenith-distance of sun.	Calculated chemical effect.	Observed effect.	Difference.	Δ%
76° 30′	9·2	5·5	+3·7	+40·0
73° 49′	16·3	15·5	+0·8	4·9
71° 37′	24·5	22·4	+2·1	8·8
68° 34′	33·1	26·2	+6·9	21·0
—	—	27·9	+5·2	15·7
67° 30′	36·6	38·9	−2·3	− 6·4
64° 42′	47·9	45·9	+2·0	+ 4·2
60° 48′	58·3	62·6	−4·3	− 7·5
58° 35′	67·9	63·1	+4·8	+ 7·1
50° 51′	85·8	89·2	−3·4	+ 4·0
46° 8′	96·4	93·0	+3·4	+ 3·5

spectrum, from about 516 $\mu\mu$ to 370 $\mu\mu$, according to Bunsen

[1] If the absorption of water vapour is allowed for, the expression would have the form $I = I_0 \, 10^{-\frac{aP + bf}{750}}$, where f is the vapour-pressure of water, b a constant. Further, it is only permissible to neglect the earth's curvature for altitudes of the sun greater than 10°. Below that the thickness must be calculated by Bouguer's formula, or that of Laplace, according to which the relative thickness is proportional to the refraction divided by sin ϕ (*vide* A. Londe, *Actinometrie*, p. 12).

and Roscoe's experiments, but it will be seen from Langley's numbers (p. 110) that it is just in this region that the selective absorption of the atmosphere is most evident. Bunsen and Roscoe themselves fully recognized that the rays of different colour within the portion of the spectrum acting were differently absorbed by the atmosphere. Thus they state, with regard to their determination of the relative action of the rays of the solar spectrum on the hydrogen-chlorine mixture, that "the experiments communicated only hold therefore for sunlight which has traversed a layer of air 9647 m. thick at 0° and 760. For layers of air of other thickness the relation between the chemical activity of the different spectral colours must be a different one."

The approximate validity for heterogeneous light of a relation theoretically true only for monochromatic radiation may be compared with the case of E. Rasch's expression for the dependence of the optical intensity, *i.e.* physiological sensation of light, on the temperature of the radiator (see p. 68). As was stated, this relation, found valid for the total brightness or for that of broad spectral regions, is identical in form with Wien's radiation function, and should therefore only apply to monochromatic illumination. The reason of this validity is probably the same in both cases, viz. the narrowness of the spectral region of maximum activity.[1]

By means of this expression, we can, following Bunsen and Roscoe, calculate the magnitude of the chemical power of the sun's rays[2] in a clear atmosphere for every geographically determined place, for every time, and for every altitude above sea-level. Assuming that the chemical effect in the actinometer is proportional to the intensity of the illumination, the formula for the chemical effect may be written—

$$W_t = W_e \, 10^{-\frac{ah\,P}{\cos\phi P_o}}$$

P_o being the height of the barometer for which the constants a and W_e were determined, P any given barometric pressure. W_e is of course the extra-terrestrial photo-chemical effect,

[1] Schaum makes it rest on the different action of rods and cones.

[2] It must be remembered that this only refers to the chemical effect of one particular actinometer, *i.e.* for one group of rays of the spectrum.

analogous to the extra-terrestrial solar-constant R_e. Bunsen and Roscoe obtained from their experiments the value—

$$W_t = 318{\cdot}3 \times 10^{-\frac{0{\cdot}4758P}{\cos\phi}}$$

i.e. $W_e = 318{\cdot}3$ light-degrees, a light-degree being 1000 light-units.

Bunsen and Roscoe defined their *chemical light-unit* as the action which their *normal* flame (*vide* p. 85) exerted at 1 metre in 1 minute on a *normal* mixture [1] of hydrogen and chlorine exposed in an insolation vessel so thin that the variation of absorption of different rays could be neglected.

The chemical illumination of the sun's rays outside the earth's atmosphere is therefore equal to $318{\cdot}3 \times 10^3$ light-units. This effect can be expressed in terms of the volume of HCl produced, or as the height of a uniform layer of hydrochoric acid gas at 0° and 760. If the rays producing this illumination are supposed to traverse an infinitely thick layer of the hydrogen-chlorine mixture till completely absorbed, they would produce a layer of HCl having at 0° and 760 a height H_1, which may be calculated by the following formula—

$$H_1 = \frac{v}{q} \cdot \frac{L}{1 - 10^{-ah}}$$

Here, v = volume of HCl at 0° and 760 produced by one light-unit,

q = surface of gas in the insolation vessel,

h = the thickness of the hydrogen-chlorine mixture reduced to 0° and 760,

a = the extinction coefficient of the mixture for the light acting,

L = the number of light-degrees.

Under the conditions for which the value 318·3 was determined, this gave $H_1 = 35{\cdot}3$ metres. Hence the extra-atmospheric sun's rays, if supposed to pass into an infinitely thick layer of the hydrogen-chlorine mixture, could unite in one minute a layer of hydrogen chlorine 35·3 metres high to hydrochloric acid. By calculation from the equation, it appears that after traversing perpendicularly the atmosphere

[1] Hydrogen and chlorine in equivalent proportions by electrolysis of HClaq.

at 760 mms. pressure, the rays only exert an action equal to 14·4 metres of the gas layer, so that two-thirds of their chemical intensity is lost by absorption and scatter.

It must be remembered that this diminution only holds for the particular reaction in question.

Consequently, the absolute deductions of Bunsen and Roscoe are of less value than the relative ones as to the distribution of the sun's chemical intensity according to barometric pressure (hence, height above sea-level) and geographical position. Their significance for meteorology is fundamental; for agricultural economy it would be greater if we could be certain that deductions made from the behaviour of the hydrogen-chlorine actinometer could be applied to the photo-synthesis in plants, which is accomplished by quite a different portion of the sun's spectrum. However, the data afforded by the hydrogen chlorine actinometer and the silver-chloride one (*vide* p. 132) run approximately in congruence, and, as will be pointed out later, the former instrument as used by Bunsen and Roscoe is perhaps the freest from errors in working and the most trustworthy.

With respect to what may be termed the photo-chemical climate, a remark of Bunsen and Roscoe's is worthy of note.[1] They point out that the law according to which the thermal climate of a place should depend upon its height above sea-level and the position of the sun is completely obscured, in that convection by sea and air leads to a quite irregular distribution. To such disturbing influences the photo-chemical climate is presumably not subject, for the local photo-chemical effect of the sun's rays cannot spread to other portions of the earth's surface. Hence the distribution of the photo-chemical forces on the earth should follow much simpler laws than the distribution of heat from the sun.

The following table gives the relative chemical illumination for different zenith-distances of the sun and heights of the barometer, calculated from the formula on p. 119. The

[1] *Pogg. Ann.*, **108**, 250, 1859. But the simplicity of these laws is obscured actually by the *other* meteorological factors, in that cloud formation interpolates a very variable factor (*vide* p. 127).

relative illumination is expressed in *light-degrees*. The upper horizontal column gives the zenith-distance of the sun, the first vertical column the height of the barometer.

TABLE XI.

M.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
0·80	132·5	130·7	125·2	115·7	102·3	81·4	55·2	24·5	2·1	0·0
0·75	139·8	138·2	132·7	123·2	108·9	88·1	61·5	28·8	2·8	0·0
0·70	147·8	146·1	140·7	131·3	116·9	96·5	68·7	33·8	3·8	0·0
0·65	156·2	154·5	146·6	139·6	125:7	105·2	76·6	29·2	5·3	0·0
0·60	165·0	163·3	158·1	149·0	135·0	114·5	85·5	46·6	7·2	0·0
0·55	174·2	172·6	167·6	158·7	145·0	124·7	95·4	54·7	9·9	0·0
0·50	184·1	182·5	177·7	169·0	155·7	135·7	106·4	64·2	13·6	0·0
0·45	194·4	193·0	188·4	180·1	167·2	147·8	118·8	75·3	18·6	0·0
0·40	205·3	204·0	199·6	191·9	179·7	161·0	132·5	88·4	25·5	0·0
0·35	216·9	215·7	211·6	204·4	193·0	175·3	147·8	103·8	35·0	0·0
0·30	229·1	228·0	224·4	217·8	207·2	190·9	165·0	121·7	48·0	0·0
0·25	241·9	241·0	237·8	231·9	222·6	207·9	184·1	142·9	65·8	0·0
0·20	255·7	254·8	252·1	247·2	239·1	226·3	205·3	167·7	90·1	0·0
0·15	269·5	269·4	267·3	263·2	256·8	246·5	229·1	196·9	123·5	0·0
0·10	285·2	284·7	283·2	280·5	275·8	268·4	255·7	231·1	169·3	0·0
0·05	301·3	301·0	300·2	298·7	296·3	292·2	285·2	271·1	232·1	0·0
0·00	318·3	318·3	318·3	318·3	318·3	318·3	318·3	318·3	318·3	0·0

The curves (Fig. 22) represent graphically the dependence

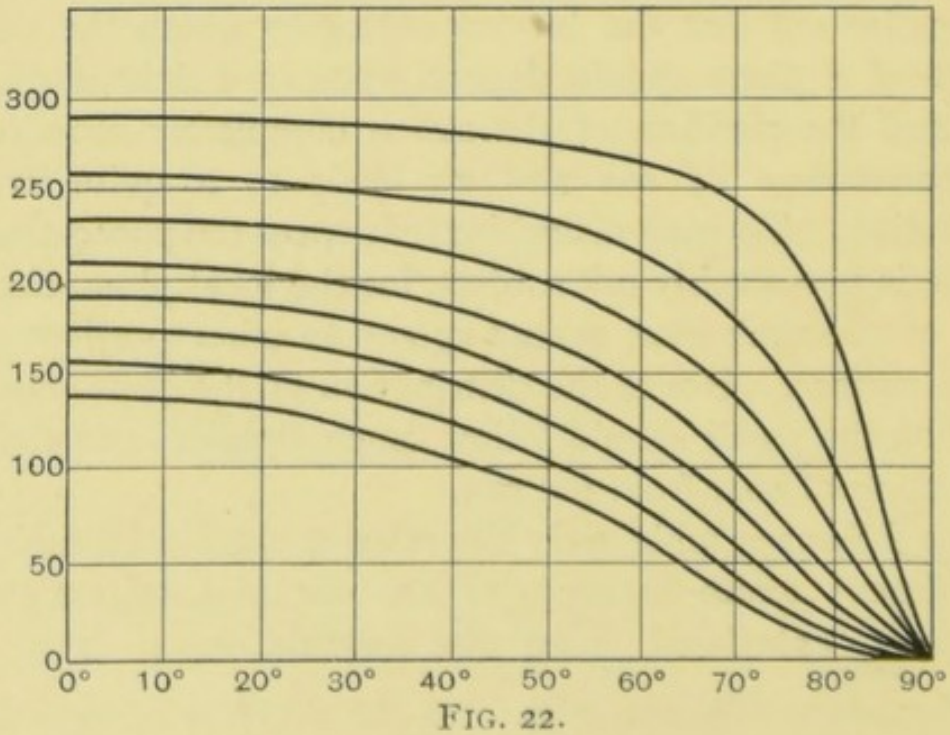


FIG. 22.

of the chemical illumination on the barometric pressure. They

show how different the chemical action in the highlands and lowlands must be under otherwise similar conditions.[1] Yet these differences, conditioned by height above sea-level, are small compared to those dependent on the geographical latitude. The formula $W_t = 318{\cdot}3 \times 10^{-\frac{0{\cdot}4758P}{\cos\phi}}$ gives the chemical illumination for a surface-element on which the sun's rays are perpendicularly incident.[2] To obtain the action on a horizontal surface element, *i.e.* one in the plane of the horizon, the values must be multiplied by cos ϕ. The following table gives the values calculated by this means by Bunsen and Roscoe for a number of places and times :—

TABLE XII.

Time.	Melville island.	Reykjavik.	Petersburg.	Manchester.	Heidelberg.	Naples.	Cairo.
6 a.m. or 6 p.m.	0·00	0·00	0·00	0·00	0·00	0·00	0·00
7 ,, 5 ,,	0·00	0·02	0·07	0·22	0·38	0·89	1·74
8 ,, 4 ,,	0·07	1·53	2·88	5·85	8·02	13·31	20·12
9 ,, 3 ,,	0·67	6·62	10·74	18·71	23·99	35·88	50·01
10 ,, 2 ,,	1·86	13·27	20·26	32·91	40·94	58·46	78·61
11 ,, 1 ,,	3·02	18·60	27·55	43·34	53·19	74·37	98·33
12 ,,	3·51	20·60	30·26	47·15	57·62	80·07	105·3

In their further investigations, Bunsen and Roscoe used for the chemical effect of the sun's rays on a horizontal surface-element, instead of this formula, $W_1 = \cos\phi \times 318{\cdot}3 \times 10^{-\frac{0{\cdot}4758P}{\cos\phi}}$, a purely empirical one, in which W_1 is expressed by a series of powers of the cosine of the zenith-distance ϕ.

$$W_1 = a\cos^2\phi + b\cos^3\phi + c\cos^4\phi.$$

[1] R. Bunsen and H. Roscoe, *Pogg. Ann.*, **108**, 270 (1859).

[2] Plants react to the change of the sun's altitude, in that the leaves are usually so turned that the upper surface is perpendicular to the sun's rays (positive heliotropism). But certain plants, to protect themselves against too intense radiation, have their leaves vertical so as to be illuminated by the morning and evening sun only. The tropisms and taxes of plants exhibit their life as in exquisite sympathy with the variations of electromagnetic energy, of which they form, so to speak, sympathetic receiving stations and reserve capacities.

§ 52. Diffused Daylight.

Direct sunlight only forms part of the light flooding the surface of the earth. In its passage through the earth's atmosphere, sunlight is not only absorbed *in* the particles composing this, whether gas molecules, dust particles, or suspended discrete water droplets, but is also reflected and reflected again from these. The *total* reduction in strength of the sun's rays is due, therefore, to both these causes. But a large part of this scattered light, as the diffusely reflected portion is termed, reaches the earth again and forms diffuse skylight. We are dealing, of course, only with a clear sky. The scattering action of the particles, when they are small compared with the wave-lengths of light, modifies the colour and quality of the total light. The longer waves dodge round, the shorter are reflected back. Supposing these shorter waves to be again reflected to earth, we should expect this skylight to be comparatively rich in the short wave-lengths. But it has itself again to pass through a certain layer of the atmosphere, and this transmission exercises a further modification, in that of its own ensemble of wave-lengths the longer are relatively impeded. Consequently its ultimate colour will be that of the intermediate wave-lengths, in the blue and green regions of the spectrum. Lord Rayleigh,[1] to whom this explanation of the blue colour of skylight is due, showed that the intensity of the scattered light varies inversely as the fourth power of the wave-length, *i.e.*—

$$I_s = \frac{A}{\lambda^4}$$

This scattered light undergoes transmission, through, say, a thickness x, so that the intensity of the light transmitted after undergoing scattering and absorption in the total thickness x, is given by—

$$I = I_s e^{-\frac{Kx}{\lambda^4}} \text{ (\textit{vide} p. 145)},$$

whence, substituting for I_s—

$$I = \frac{A}{\lambda^4} \cdot e^{-\frac{Kx}{\lambda^4}}$$

[1] *Phil. Mag.*, **41**, 107, 275 (1871).

which expresses both the effects of scattering and absorption on any ray.[1]

Another result of the scattering or diffuse reflection is that the light from the sky is polarized, to a degree depending upon the altitude of the sun. It can, therefore, be extinguished by reflection, and this has to be taken account of in determining either its chemical or optical intensity. The light should, when possible, be allowed to act directly, not by reflection, on the receiving surface. For a full account of the absorption and polarization of light by foggy or turbid media, and their dependence on the size, etc., of the particles, see G. Mie, *Ann. Phys.*, **25** (3), 377 (1908).

Rayleigh's theory has frequently been called in question,[2] and specific absorption by components of the atmosphere (O_2, O_3, H_2O_2) allotted a part in determining the colour of skylight. For a comprehensive review of the entire question a paper by G. L. Nichols may be consulted.[3] The latter, from spectrophotometric observations, finds a greater variability in the extreme violet and red.

The total illumination due to the diffused light alone depends of course on the position of the sun, and the measurement of its chemical intensity offers considerable experimental difficulty. Bunsen and Roscoe determined it indirectly as follows:[4] They measured photometrically the *ratio* of the illumination on a horizontal surface element due to the whole sky to that due to a portion at the zenith $\frac{1}{1000}$ of the total, throughout the day on clear days, the direct sunlight being diverted. If we term I_t the illumination due to the whole sky, and I_z that due to the zenith portion, then they determined the variation of $\frac{I_t}{I_z}$ with the sun's altitude. They found that this ratio was a linear function of the zenith distance, *i.e.*—

[1] See A. Schuster, *Astrophys. Journ.*, **26**, 1 (1905) for a complete mathematical treatment of the effect of a "foggy" atmosphere on radiation.

[2] Spring, *Bull. Acad. Belge*, [3] **36**, 504; W. H. Hartley, *Nature*, **39**, 474 (1889).

[3] *Phys. Rev.*, **26**, 497 (1908).

[4] *Pogg. Ann.*, **101**, 213 (1859); Ostwald's *Klassiker*, **38**, pp. 48 *et seq.*

$$\frac{I_t}{I_z} = a + b\phi$$

values both before and after noon agreeing. This pointed to little variation in the *optical* transparency of the atmosphere in clear weather, although the temperature and hygrometric state varied considerably.[1] They then determined under similar conditions the *chemical* intensity for the chlorine-hydrogen actinometer of a portion of the sky at the zenith $\frac{1}{1000}$ of the total. Calling this w, it was found that the relation of w to the sun's altitude could be satisfactorily expressed by the equation—

$$w = a_1 - b_1 \phi + \frac{c_3}{\phi}$$

ϕ being the zenith distance as before. Since for *one and the same light-source* the optical and chemical intensities are proportional, then the value of w_1, the chemical intensity of the total skylight, could be obtained by multiplying the values of $\frac{I_t}{I_z}$ by the corresponding value of w for the same altitude of the sun. The values of w_1 thus found, they expressed as a function of the sun's altitude by the series

$$w_1 = a + b \cos \phi + c \cos^2 \phi$$

The total effect over a given period of time of the diffused light may be obtained by integration of this function for the given time interval $t' - t''$

$$W = \frac{12 \times 60}{\pi} \int_{t'}^{t''} w_1 dt$$

the angular time being expressed in radians, or by planimetry of the curves of diurnal variation.

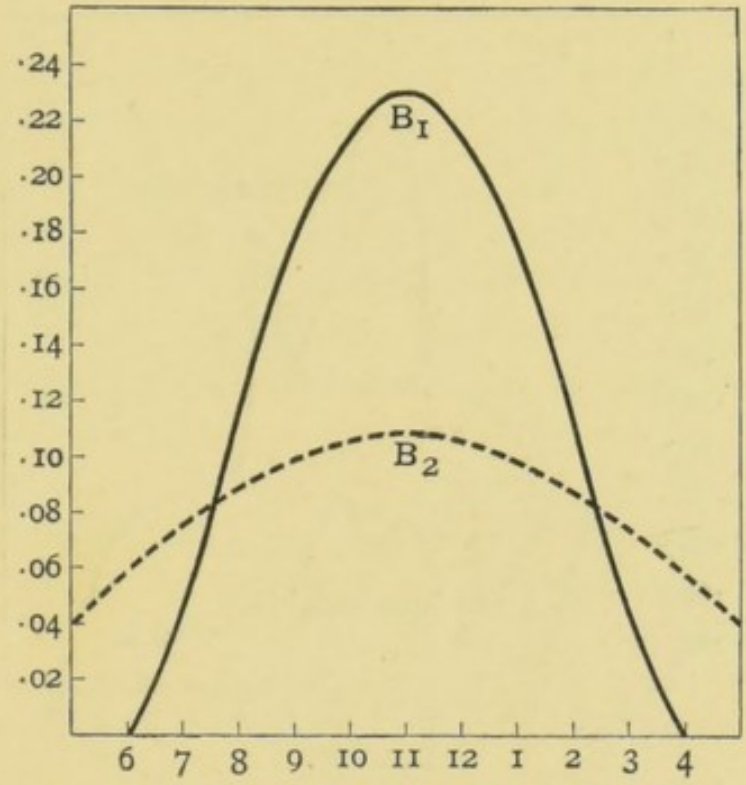
§ 53. Phases of Equal Illumination.

A comparison of the equations and tables for the direct and diffused light repectively shows that for all places where the sun rises more than 21° above the horizon, the *diffused*

[1] Later experiments on the total intensity show that this statement must be considerably modified.

daylight has *greater* chemical power than the direct sunlight from sunrise onward until the sun reaches a certain height, after which the latter is more intense. The phases of equal chemical intensity, as Bunsen and Roscoe termed them, which occur twice daily, may be determined for a given zenith-distance ϕ by equating the formulæ for the respective actions of the direct and diffuse light.

By means of this formula the chemical illumination due to



B_1 represents the variation of direct sunlight.
B_2 ,, ,, ,, diffused light.

FIG. 23.

the total unclouded skylight can be calculated for any geographically determined place and time.

Bunsen and Roscoe subsequently abandoned the hydrogen-chlorine actinometer in favour of the more adaptable "normal tone" silver chloride paper, and with this determined the daily variation of the total chemical intensity, *i.e.* of the direct sunlight *plus* skylight, on a horizontal surface element. Roscoe further[1] perfected the method and carried out a series of determinations in 1863–1864, the mean diurnal chemical

[1] Cf. A. Londe, *L'Actinométrie*, p. 220.

illumination being obtained by planimetric integration of the curve. The uniform action of light of intensity 1 during 24 hours was taken as 1000. How much the chemical intensity may vary from day to day as the atmospheric conditions change is shown by the curves in Fig. 24.

The mean intensity on June 20 was less than half that on June 22, the values being as 50·9 : 119 = 1 : 2·34.

The sudden changes in intensity shown in this curve are

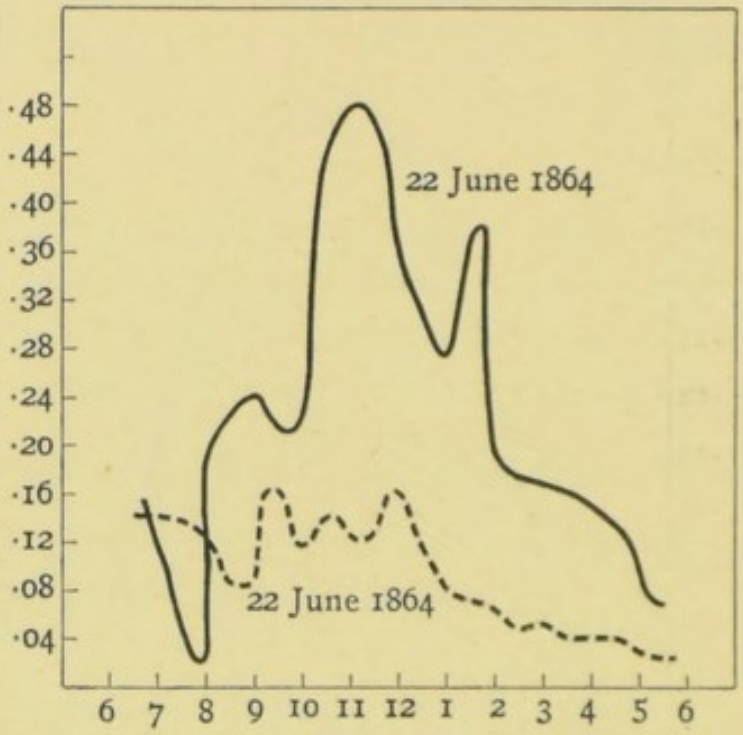


FIG. 24.

not necessarily produced by condensation visible to the eye, as they occur when the heavens remain cloudless. Roscoe attributed them to a fine precipitation, since his observations showed that a light mist, hardly noticeable to the eye, exercised a very great absorbing power on the chemically active rays. Simultaneous observations of the barometer and psychrometer show there is no simple relation between the chemical intensity and the vapour pressure. Vogel,[1] therefore, concludes that it is not water as gas but as droplets, not necessarily united as cloud, which has the greater influence on the chemical transparency of the atmosphere.

[1] *Pogg. Ann*, **156**, 319.

By means of the "normal" silver chloride paper actinometer Roscoe[1] made a comparison of the action of the total daylight and of the diffuse light alone. Clausius,[2] on the assumption that the scattering and diffusion of light was due not to reflection from dust particles or air molecules, but from water droplets, has calculated the relative optical intensities for different heights of the sun of the direct and diffuse radiation. Roscoe compared his results with these, and found that quite different relations held for the chemically active rays. Generally he found—

(*a*) That the influence of the atmosphere on the more refrangible and chemically active rays is regulated by laws quite different from those which would follow from the hypothesis of reflection by small water-drops.

(*b*) The relation of the chemical intensity of direct sunlight to the diffuse skylight for a given height of the sun at different places is not constant, but varies with the transparency of the atmosphere.

(*c*) This relation is quite different from that of the relative optical intensities; thus the atmosphere has an effect 17·4 times as great on the chemically perceived rays[3] as on the visible ones for an altitude of the sun of 26° 16′, and 26·4 times as great, for an altitude of 12° 3′.

The relation of the integral chemical intensity of daylight to the altitude of the sun on clear days was found to be well represented by a linear equation of the form—

$$W_a = W_o + h \times constant$$

where W_a is the effect at an altitude a,
and W_o „ „ „ o,
except for when the sun was only a few degrees above the horizon, since at that time opalescence due to dust had a very disturbing effect. Further measurements, both of the total daylight and of the diffuse light, were carried out by Roscoe and

[1] *Pogg. Ann.*, **132**, 404.
[2] *Ibid.*, **76**, 161; and **84**, 449 (1849).
[3] That is, those which affect silver chloride paper (*vide* p. 132).

T. E. Thorpe, on the west coast of Portugal,[1] and careful notice taken of the meteorological conditions. The above formula was again found valid for clear days. The curve for direct sunlight alone cut the axis at 10°, confirming Roscoe's previous datum, that the chemical action of the sun below 10° is practically nil. Taking from their table of mean results, the values for times equidistant from midday, we have the following table :—

TABLE XII.

No. of observations.	Height of sun.	Sun.	Chemical intensity. Diffuse.	Total.	Calc. total.
15	9° 51′	0·00	0·038	0·038	0·035
18	19° 41′	0·023	0·062	0·085	0·089
22	31° 14′	0·052	0·100	0·152	0·154
22	42° 13′	0·100	0·115	0·215	0·215
19	53° 7′	0·136	0·126	0·262	0·275
24	61° 8′	0·195	0·132	0·327	0·320
11	64° 14′	0·221	0·138	0·359	0·337

The direct sunlight was obtained by difference between the values for the total and the diffuse light. These measurements again illustrate the " phase of equal chemical intensity " of the sun- and diffuse light (p. 127). The calculated values for the total intensity were obtained by the formula—

$$W_a = W_o + h \times constant$$

which was found valid for observations at Heidelberg, Kew and Para also, but with different values for the constant, which expresses the inclination of the straight line. This difference was ascribed by Roscoe to a locally varying atmospheric opalescence. An extended series of observations with the " normal-tone " actinometer made by E. Stebbing[2] in 1874–1875 at Petersburg, were chiefly directed to the study of weather conditions. The only actinometric research comparable in extent with those of Bunsen and Roscoe, or of

[1] *Phil. Trans.*, 1870, p. 309 ; *Pogg. Ann.* (Erganzungs Bd.), V. 177.
[2] *Zeitschr. d. österr. Ges. f. Meteorologie*, **14**, 43.

others made by their methods, is that of Marchand,[1] 1869–1870, made at Fécamp, who employed an aqueous solution of ferric chloride and oxalic acid. In the actinometric arrangement to which he applied the fearsome polysyllable "photantitupimeter,[2] the intensity was measured in terms of the volume of CO_2 evolved, reduced to 0° and 760 mm. The total effect of the direct sunlight and the diffused light on a horizontal surface he expressed by the more or less empirical formula—

$$W_s + W_d = ah - bh^2$$

where h is the altitude of the sun.

In all these investigations, the intensity measured was that of the violet and ultra-violet part of the spectrum, though with ferric oxalate the action extends into the blue-violet. The all-important photo-chemical synthesis in green plants is effected by quite a different part of the spectrum, corresponding in fact to the absorption-spectrum of the chlorophyll, and it becomes very doubtful if the conclusions drawn from Bunsen and Roscoe's and other similar observations as to the photo-chemical "climate"[3] can be profitably applied in this connection. The same may be said for photography by means of plates sensitive beyond the blue; so-called ortho-iso-, and panchromatic plates. From the optical measurements of H. C. Vogel[4] and E. Köttgen[5] we know that the relative brightness of different parts of the spectrum varies considerably with atmospheric changes. J. Precht and E. Stenger[6] find with panchromatic plates a considerable variation in the relative actions of three divisions of the spectrum (blue λ = 410–490, green λ = 505–580, orange λ = 570–725), according to the time of the year, of the day and the atmospheric transparency, which may be expressed in general by saying that

[1] G. Marchand, "*Étude sur la force chimique contenue dans la lumière du soleil*" (Paris, Gauthier-Villars).

[2] From "antitopia" = movement of reaction.

[3] See p. 121.

[4] *Ber. Berl. Akad.*, 1880, 801.

[5] *Wied. Ann.*, **53**, 793 (1894).

[6] *Zeit. wiss. Phot.*, **3**, 27 (1905).

with decreasing total intensity of light the actions in the red and green fall off much more rapidly than that in the blue. All the more valuable, then, is the application made by Andresen[1] of Bunsen and Roscoe's "normal tone" actinometer to the measurement of the chemical intensity of other regions of the sun's spectrum. Andresen uses silver bromide paper sensitized with different dyes, amongst others chlorophyll. With this he has determined the absorption of direct sunlight for different parts of the spectrum, using the formula—

$$W_t = W_e \, 10^{-\frac{aP}{\cos \phi}}$$

and obtained the following results :—

Region of spectrum.	Sensitive paper.	W_e.	a.	Absorption on 1ar transmission.
Violet and ultra-violet, max. bet. F and G	AgCl	4715	0·296	40·5%
Near D, max. of visual luminosity	AgBr erythrosin	1663	0·109	17%
Red end, beyond 610 $\mu\mu$	AgBr, with rhodamine and rhododendron chlorophyll	445	0·117	18·7%

§ 54. Summary and Criticism of the Quantitative Relations.

For *direct sunlight* the dependence of the chemical intensity on the sun's altitude and the barometric pressure is given by—

$$W_t = W_e \times 10^{-\frac{aP}{\cos \phi}}$$

where ϕ is the sun's zenith-distance. The chemical illumination of a *horizontal* surface element may be expressed by—

$$W_s = a \cos^2 \phi + b \cos^3 \phi + c \cos^4 \phi$$

For *diffuse daylight* on clear days, the action of the

[1] M. Andresen, Eder's *Jahrb. f. Phot.*, 1899, p. 147.

illumination of a horizontal surface element was found to be representable by the function (p. 126)—

$$W_d = a_1 + b_1 \cos \phi + c_1 \cos^2 \phi$$

according to Bunsen and Roscoe. E. Hertzsprung[1] finds for the decline in the illumination due to the diffuse light as the sun's height decreases—

$$\log \frac{W_o}{W_\phi} = a - b \operatorname{cosec} \frac{\phi}{2}$$

where W_o = action at midday,
W_ϕ = action for zenith-distance ϕ.

Finally, for the total chemical intensity on a horizontal element due both to the direct sun and the diffuse light, we get from Roscoe's work—

(*a*) The normal chemical intensity of the total daylight is a function of the sun's height, the equation expressing the diurnal variation being a straight line—

$$W_k = W_o + h \times \textit{constant}.$$

(*b*) The maximum is therefore at midday, the action equal at hours equidistant from noon.

(*c*) The constants W_o and *const.* alter according to the place and time.

Pernter[2] in a comprehensive review of Bunsen and Roscoe's, also of Marchand's results, but especially of Roscoe's Portuguese data,[3] concluded that whilst the equation (*a*) held satisfactorily before noon, after noon deviations of a steady type might occur. Further, the maximum did not always fall at noon, being in some localities regularly advanced, in others retarded.

However, the law of the meridional maximum has been confirmed by Wiener for Vienna, and Fr. Schwab[4] at Kremsmünden. Pernter concluded that the constants of the linear equation are actually functions of the hygrometric state of the atmosphere and every condition influencing its transparency,

[1] *Zeit. wiss. Phot.*, **4**, 109 (1906).

[2] *Zeitschr. d. österr. Ges. f. Meteorologie*, 1879, pp. 2101 *et seq.*

[3] *Phil. Trans.*, **169**, 472 (1871).

[4] On the photochemical clime of Kremsmünden, *Oesterr. Chem. Zeit.*, 1903, p. 325.

whereby its general value is greatly lessened. The daily curves of chemical intensity seem just as little susceptible of formulation by a simple function of the sun's altitude as those of temperature. The nearest approach is made by the linear law, but it appears impossible to express in one equation the normal chemical intensity for every latitude at different times of the day and year. A critical analysis, which as far as I know has not yet been made, of data compiled since Pernter's review (1879) must decide whether this somewhat pessimistic conclusion is wholly justified. As tending to confirm the existence of regularities, though locally influenced, we may note that the law of phases of equivalent illumination was confirmed by Wiener at Vienna, by Schwab at Kremsmünden whilst L. Weber's [1] observations at Kiel, extending over thirteen years, and H. König's at New Brandenburg,[2] point to the quality of the total daylight at noon (direct sun *plus* diffuse) being approximately independent of the time of year.

As already pointed out, practically all this investigation is concerned only with the ultra-violet, and the variable and disturbing factor—apart from absolute clouds—is the variation of the transparency of the atmosphere for these rays. Now it appears quite possible that it is just for these shorter wavelengths that the variation is a maximum, and that for other parts of the spectrum, also chemically effective,[3] that the variation is much less. The transparency to the ultra-violet appears to depend chiefly on the presence of condensed water particles. Condensation produced by the cooling due to expansion occurs much more readily in nucleated air than in air free from nuclei.

Aitken,[4] whose work in this connection has been of fundamental importance, consider that dust alone is sufficient to account for atmospheric condensation. On the other hand, Arrhenius [5] and Elster and Geitel [6] consider that nucleation

[1] *Schriften d. Natur wiss. Ver. f. Schleswig-Holstein*, **10**, 77 (1903).
[2] See A. Londe, *L'Actinomètric*, p. 153.
[3] Practically up to 1000 $\mu\mu$.
[4] *Nature*, 1900, 514.
[5] Sv. Arrhenius, *Meteorol. Zeit.*, 1888, p. 297.
[6] Elster and Geitel, *Wien. Sitz. ber.*, **101** [2], 703 (1892).

by ions plays an important *rôle*; the latter are inclined to attribute the ionization chiefly to the discharge of negative electricity by ultra-violet light at the earth's surface, Arrhenius to the direct ionization of moist air by ultra-violet light. Inasmuch as the nucleation of dust-free air by radiation is a definite fact,[1] and that the sun's radiation outside the atmosphere must be far richer in ultra-violet, his view has much to commend it. Such an action would bring about, as it were, an auto-catalysis of the absorption of ultra-violet light by the atmosphere. Another variable factor in this connection is the ozone-content of the atmosphere, since the reaction $2O_3 \rightleftarrows 3O_2$ is affected by ultra-violet light (*vide* Chap. VI.). The important point is the probability of a specifically greater variability in the intensity of the ultra-violet region compared with other parts of the spectrum. It would be desirable to have extended actinometric measurements with Elster and Geitel's photo-electric photometer,[2] and also with actinometers based on Andresen's method. It may be that greater regularities will be found, justifying to some extent Bunsen and Roscoe's conception of the simplicity of the laws regulating the photochemical climate, although not solely for the radiation which they chiefly investigated.

For a paper dealing with the rules to be observed in applying actinometry to meteorology, see J. Sebelier,[3] and on the application of actinographic tables for photographic purposes, compare J. Beck.[4]

[1] The subject is of great importance for photochemistry, and is dealt with later; see Chap. VII. Cf. C. Barus, *Ann. Physik.*, [4] **24**, 225 (1907), for recent work on the question.

[2] J. Elster and E. Geitel, Eder's *Jahrbuch*, 1906, p. 39; see also Chap. VII.

[3] Eder's *Jahb.*, 1905, p. 351; *Chem. Zeit.*, 1904, p. 423.

[4] *Ibid.*, 1904, p. 156.

CHAPTER V

THE ABSORPTION OF LIGHT

§ 55. Definitions.

The absorption of light by material media is necessarily described mathematically by relations—idiograms, one might term such generalized mnemonics—identical in form to those valid for the absorption of wave-motion in general by media of texture commensurable with the periods of the movement. This is of course following the assumption that *light* corresponds to a vibratory motion of the hypothetical æther of space. What principally affects and modifies the form of the mathematical functions expressing the constants of the absorption is the complexity of the interrelation or correlation of the wave-length with the amplitude and the form or shape-factor of the waves, seeing that in dealing with absorption—and, conversely, with emission, we have to make certain assumptions as to the interaction of the imponderable æther with ponderable matter.

We may as a first approximation distinguish two principal types of vibratory or wave-motion in a homogeneous medium, the waves being supposed to start from and spread out about an assigned (arbitrary) origin ; these two types are distinguished according as the amplitude of the disturbance falls off *directly* as the distance from the origin, or as some power of the distance—for example, the square.

Vibrations for which the first condition holds are termed "transverse," because the to-and-fro movement or displacement of the particles or force-centres of the medium transmitting the disturbance are perpendicular to the principal direction of propagation of the head of force or velocity-potential of the change. A large number of the phenomena of interference

and polarization agree with the assumption that in polarized light-rays of definite periodicity or oscillation-frequency we are dealing with transverse vibrations of the æther. On the other hand, the nature of white light is apparently insusceptible of explanation by any hypothesis of a regular and regularly recurring periodic or vibratory motion of the æther. As there appear to be many analogies in behaviour between white light on the one hand and X-rays, β-rays, and γ-rays on the other, and as the nature of the latter is still *sub judice*, the alternative pronouncements in favour of incoherent æther-pulses and a type of corpuscular radiation having up to the present about equal strength, we are left with white light as the sign of, or the actuality of, a transmutation of values which our present symbolic logic seems incompetent to tackle,—as though "das Unbeschreibliche hier wird getan."[1]

Before proceeding to the mechanical and electrical conceptions which have been conceived to afford a physical explanation of the phenomena of absorption and dispersion, and of which a brief account is given in a latter portion of this chapter, we shall deduce the formulæ and expressions of principal value in recording numerical measures of the facts of absorption.

Assuming that we are dealing with the propagation of spherical waves in a homogeneous medium, the oscillations being transverse to the direction of propagation, then the intensity $\propto \frac{1}{d^2}$ at a distance d from the origin, or conversely, $\propto a^2$, where a is the amplitude of the vibration.

Then the absorption-coefficient k is defined as the reciprocal of that thickness of the medium which reduces the amplitude of a vibration to $\frac{1}{e}$ of its original value, that is, to $a_0 e^{-1}$, if a be the original amplitude.

Since the *intensity* is defined as a quantity equal to the mean square of the amplitude, the *intensity* on reduction becomes $i_0 e^{-2kd}$, when d is the thickness traversed by the

[1] Cf., however, A. Eagle on "The Form of the Pulses constituting Full Radiation, or White Light," *Phil. Mag.*, [6] **18**, 787 (1909).

vibration, and k is the *specific* absorption-coefficient for that medium of that vibration.

But it is often desirable to measure in *critical* units, and since in very strong absorptions the thickness which reduces the intensity to zero value (extinction) is only a few wave-lengths, the *extinction-index* is defined in terms of the *critical* ordinate of that kind of light employed, viz. its wave-length when measured *in vacuo*.

Hence we have a similar proposition to the first. The amplitude is reduced to $a_0 e^{-\frac{2\pi\chi}{\lambda}}$ on traversing a thickness equivalent to λ, the wave-length of the vibration *in vacuo*. Hence similarly the intensity is reduced to $i_0 e^{-\frac{4\pi\chi}{\lambda}}$ for a thickness equivalent to λ, or for any thickness d to $i_0 e^{-\frac{4\pi\chi d}{\lambda}}$. χ is the reduced specific absorption-constant, or, as it is more briefly termed, the extinction-index. If we put $e^{-\frac{4\pi\chi d}{\lambda}} = e^{-2kd}$ (since these betoken an identical diminution of intensity), we see that—

$$\chi = \frac{\lambda k}{2\pi}$$

There is another reduced value possible, which involves the more problematical value l, the *inner* wave-length of the vibration in a substance supposed heterogeneous with that in which the vibration originates. As before, the amplitude is reduced for a depth d to $a_0 e^{-\frac{2\pi\chi'}{e}}$. This χ' is then equal to $\chi\nu$, where ν is the index of refraction of the light betwixt the discontinuity of the medium. If c_0 be the velocity of light *in vacuo*, and c its velocity in the second medium, then—

$$\nu = \frac{c_0}{c} = \frac{\lambda}{l}$$

Whilst for transparent substances in which no absorption occurs, ν, the refractive-index, is independent of the angle of incidence of the ray, this ceases to be the case when there is absorption, which is always concomitant with a certain internal catastrophe and phase-change of the incident vibrations,

depending implicitly upon the angles of incidence of the rays. The foregoing definitions of the absorption-constants are expressly defined as valid for normal or perpendicular incidence only. If we call the angle of refraction $\hat{r}$ (that is, the angle between the refracted ray and the normal to the surface), then this $\hat{r}$ is also the angle between *planes* of equal *amplitude* and planes of equal *phase* in the refracted beam,[1] and both χ and ν depend upon $\hat{r}$. Generally, χ_0 and ν_0, the values when $\hat{r} = 0$, are related to other values, by the conditions—

$$\nu_r^2 - \chi_r^2 = \nu_0^2 - \chi_0^2$$
$$\nu_r^2 \chi_r^2 \cos \hat{r} = \nu_0^2 \chi_0^2$$

and χ and ν, the extinction-index and the refractive-index, are the most important photochemical constants of any particular substance with regard to any specific vibration.

§ 56. The Absorption of Light.

In Kirchhoff's law correlating emission and absorption, we have a gross relation dealing with matter abstracted from all those specific qualities which constitute the individuality of substances, the investigation of which is the peculiar province of chemistry. We have seen how little any chemically individual substance fulfils the definition of a black body. And just as in reality there are no all-absorbing bodies, so there are no perfectly transparent substances. Whilst some, as the metals, even in very thin sections, are practically opaque to ordinary light, others, as glass, are very transparent. But these terms are purely relative, since they depend upon the quality and wave-length of the radiation. Water, which is very transparent to the visible rays, and to the ultra-violet up to 200 $\mu\mu$, has a strong absorption for the long waves in the infra-red. Always more or less selective, the absorption of light is the prime factor in the creation of colour. Moreover, anticipating a later section, we may note its fundamental importance for photo-chemistry, in that *only the light which is absorbed is active in producing chemical change.* This is usually known as Draper's

[1] Cf. H. Kayser, *Hdbuch. d Spektroskopie*, vol. v., Art. "Dispersion."

law,[1] but was first definitely formulated by Grotthus in 1818.[2] Imbued as we are now with the notions of conservation of mass and conservation of energy, there appears something axiomatic in this statement, yet in view of so-called "catalytic light actions" (*vide* Chap. VII.), the proposition is not so self-evident as one might think. Although the converse—that all light which is absorbed gives rise to chemical action—is non-proven, the absorption-spectrum of a chemical system is intimately connected with its photochemical behaviour.

Bunsen and Roscoe[3] proposed the terms "achemic" and "diachemic" respectively to designate substances which absorb or transmit those shorter wave-lengths which are most chemically active, but as in the case of "athermic" and "diathermic," the terms cannot be strictly defined. The phrase "diactinc" is frequently used for substances transmitting photographically active light.

§ 57. Quantitative Relations.

It will be evident from the foregoing that these relations must be obtained for homogeneous or monochromatic light. If a ray of such light traverse an absorbing substance a certain proportion is absorbed. This fraction is independent of the original intensity, *i.e.* the amount absorbed is proportional to the incident intensity (Lambert's law).[4]

It is necessary to define the original intensity more closely. The intensity of the entering light is not equal to that which falls on the bounding surface of the absorbing substance, since a certain proportion is reflected. In the case of liquids and solutions in glass or other transparent vessels more than one reflecting surface intervenes, and the reflection has to be considered in the illumination of photochemical systems.

In the definitions of the constants of absorption which were

[1] *Phil. Mag.*, [3] **19**, 195 (1841).

[2] "The Chemical Action of Light and Electricity," Ostwald's *Klassiker*, **152**, 94.

[3] *Pogg. Ann.*, **101**, 235 (1855).

[4] J. H. Lambert, *Photometria* (1759); Ostwald's *Klassiker*, **32**, p. 66.

deduced in paragraph 55, the question as to the absolute values of the initial amplitudes—designated a_0, and the corresponding intensities, i_0—was not posed or answered, but it was noted that they depended upon conditions of incidence at the boundary of heterogeneous media, as well as upon actual damping within one medium assumed to be homogeneous. The calculation for losses by reflection at surfaces is usually made with the help of Fresnel's law of reflection.[1]

When a beam of light, considered initially as unpolarized, is reflected at a polished or lustrous surface, it becomes polarized[2] into two sets of vibrations polarized at right angles to each other, and for each of which the loss of intensity may be separately calculated.

Suppose I be the intensity of the non-polarized beam before transmission through the surface of a transparent medium, and, for the sake of simplicity, let $I = 1$. Then if i_p and i_q are the intensities of the rays polarized in and at right angles to the plane of incidence, we have

$$I = i_p + i_q = 1$$

and

$$i_p = i_q = 0{\cdot}5$$

Further, let θ be the angle of incidence of the rays, ϕ the angle of refraction, so that

$$\sin \theta = \nu \,.\, \sin \phi,$$

where ν is the refractive index of the second medium compared to the first. If we further term I_1 the total intensity of the ray-bundle after refraction at the surface, and i_{1p} and i_{1q} the intensities thereof parallel and perpendicular to the surface, supposed a plane, then, according to Fresnel's law—

$$i_{1p} = i_p\left(1 - \frac{\tan(\theta - \phi)}{\tan(\theta + \phi)}\right)$$

$$i_{1q} = i_q\left(1 - \frac{\tan(\theta - \phi)}{\tan(\theta + \phi)}\right)$$

and also

$$I = 1 - \tfrac{1}{2}\left(\frac{\tan^2(\theta - \phi)}{\tan^2(\theta + \phi)} + \frac{\sin^2(\theta - \phi)}{\sin^2(\theta + \phi)}\right)$$

[1] *Ann. de chim. et phys.*, [2] 17, p. 190 (1821).

[2] Cf. T. Preston, *Theory of Light*, p. 288 (2nd ed., 1895).

When plane-parallel surfaces of absorption-vessels, etc., are in use, it is usually the case that the ray-bundle is incident perpendicularly, in which case the angles θ and ϕ are identically equal to zero. Hence, sines and tangents can be replaced by the corresponding angles, we have $\theta = \nu\phi$, and the expression for the intensity subsequent to transmission through a surface takes the form

$$I_1 = 1 - \left(\frac{\nu - 1}{\nu + 1}\right)^2$$

When more than one surface has to be taken into account, the equations for the reduction of intensity by reflection become correspondingly complex. A frequently occurring case is that of a single glass plate with two surfaces, at which reflection and refraction occur before the ray penetrates the final medium. In this instance we have to take into consideration the multiple reflection of the ray within the plate between the two bounding surfaces.

Let the intensity of the ray penetrating the first surface be I_1. At the second surface the quantity $(1 - I_1)I_1$ is reflected, whilst I_1^2 is transmitted. The reflected rays on return to the first surface are again reflected, giving the intensity $(1 - I_1)^2 I_1$, and reach the second surface with the intensity $(1 - I_1)^2 I_1^2$. This ray is twice reflected in the interior of the plate. The ray which has undergone fourfold reflection has on escape from the plate the intensity $(1 - I_1)^4 I_1^2$, and so on, so that for the total intensity of the ray-bundle emerging from the plane-parallel plate we have the expression—

$$I_2 = I_1^2 + I_1^2(1 - I_1)^2 + I_1^2(1 - I_1)^4, \text{ etc.}$$

$$= I_1^2 \frac{1}{1 - (1 - I_1)^2} = \frac{I_1}{2 - I_1}$$

If the quantity $(1 - I_1)$ is very small, then I_2 is very near to I_1^2, otherwise the factor $\frac{1}{1 - (1 - I_1)^2}$ cannot be neglected. The calculation must naturally be made for each of the ray-bundles polarized at right angles to each other, and the results

for both added together to obtain the total intensity of the transmitted light.[1]

The absorbing power $A = \frac{I_0 - I}{I_0}$, where I_0 is the light actually entering, I that transmitted. If the reflecting factor be borne in mind, it will be simpler to consider absorption apart from this, and term the incident light I_0. Lambert's law may be stated as—

$$\frac{I}{I_0} = T$$

where T is a constant called the *transparency*. Transparencies are frequently given in percentages, $\frac{I}{I_0} \times 100$. That T is a constant for different values of I_0 was proven experimentally for the ensemble of rays affecting the hydrogen-chlorine actinometer by Bunsen and Roscoe.[2]

Coefficients of Transmission and Absorption.—It follows from Lambert's law that if the thickness of the absorbing medium increases in arithmetical progression, the light transmitted should decrease in geometrical progression. Let I be the intensity of light traversing a layer *dl*, then—

$$-\frac{dI}{dl} = kI,$$

which gives on integration, if I_0 be the original intensity, and *d* the total thickness,

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

The constant *k* is a constant depending upon the nature of the substance and the wave-length of the light. It has been variously termed the *absorption-constant*,[3] the *absorption-coefficient*,[4] and the *absorption-index*. The last term, recommended by Kayser, appears the most suitable.

[1] For details as to the experimental confirmation of such reflection-formulæ with different glasses and surfaces, see G. and H. Kruss, *Kolorimetrie und quantitative Spektralanalyse*, pp. 230 *et seq.* (Hamburg, L. Voss).

[2] *Pogg. Ann.*, **101**, 237 (1857); Oswald's *Klassiker*, **38**, 5.

[3] T. Preston, *Theory of Light*, 2nd ed., 1895, and § 55, p. 136.

[4] E. Hagen and H. Rubens, *Drude's Ann.*, **8**, 432 (1902).

It will be seen that

$$k = \frac{1}{d} \log_e \frac{I}{I_0}.$$

Writing $^{-k} = a$, we have again—

$$\frac{I}{I_0} = a^d$$

For the constant a a like variety of terms has been employed.[1] We shall follow Kayser's nomenclature and call a the *transparency* or *transmission-coefficient*.[2] Finally we must note Bunsen and Roscoe's[3] *extinction-coefficient*, which is the reciprocal of that thickness of the medium reducing the intensity to $\frac{1}{10}$ of its original value. Calling this ϵ, we have—

$$I = I_0 \, 10^{-\epsilon d}$$

$$\text{and } \epsilon = \frac{1}{d} \log_{10} \frac{I}{I_0}.$$

the relation between ϵ and k being that $e^{-k} = 10^{-\epsilon}$ or $\epsilon = mk$, where $m = log_{10} e$, the modulus of natural logarithms. As Kayser has pointed out, a standard nomenclature for the derived quantities is much to be desired. Every worker on questions of absorption seems either to have used the same terms with different meanings, or devised wholly new ones. Thus ϵ is sometimes termed the *Bunsen* or *decadic* extinction-coefficient, to distinguish it from the like named quantity of different significance in Cauchy's theory of metal optics, and which plays an important part in applications of the

[1] Cf. H. Kayser, *Hdbuch. d. Spektroskopie*, iii. 115 (1905); and R. Luther, *Zeitschr. Physik. Chem.*, **30**.

[2] For the reciprocal quantity, $\frac{I_0}{I}$, the term *opacity*, due to Hurter and Driffield (*Journ. Soc. Chem. Ind.*), is used in photographic technology, and the value $\log \frac{I}{I_0}$, corresponding to the extinction-coefficient, is termed the *density* D (Schwarzing, *Dichtigkeit*) with photographic negatives.

[3] *Loc. cit.*, p. 238; Ostwald's *Klassiker*, **88**, 6.

electromagnetic theory. However, as Rudorf[1] remarks, it is easy to judge from the context which is intended.

§ 58. The Effect of Concentration—Beer's Law.

From rather inadequate experimental material A. Beer[2] deduced that the absorption is the same function of the concentration of a dispersed absorbing substance as of the thickness of a single substance. Hence, if c be the concentration—

$$I = I_0 a^{\epsilon c l}$$

Following Beer, Vierordt[3] introduced the term *absorption-ratio* for the quantity $\frac{c}{\epsilon} = \frac{\text{concentration}}{\text{extinction-coefficient}}$, which should be a constant if Beer's law hold. The law has been the subject of much experiment, and in many cases confirmed, in others not.[4] Roughly, the position as regards solutions is as follows: following Wolfgang Ostwald,[5] we may distinguish between molecular dispersoids (true solutions) and dispersoids of a lower degree of dispersion, so-called colloid solutions. An obvious condition for the validity of the law is that no change takes place in the condition of the dispersed substance —the solute—on altering the concentration. In the first case, Beer's law is assumed as correct for one molecular species, and the question is shifted to the consideration of the cause of the deviation. To this we shall return when dealing with the absorption phenomena of solutions. In the second case—colloid solutions—it is probable that the law only holds at considerable dilutions; not only does concentration favour flocking of the particles (the equivalent of the association of discrete molecules), but the scattered or internally reflected

[1] G. Rudorf, *Ahren's Sammlung*, **9** (1 and 2), 1904, p. 15; *Jahrb. d. Elektron*, **3**, 428 (1907).

[2] A. Beer, *Pogg. Ann.*, **86**, 78 (1852).

[3] K. Vierordt, *Quantitative Spektralanalyse*, Tübingen, 1876.

[4] Cf. H. Kayser, *loc. cit.*, and G. Rudorf, *Jahrb. d. Elektron, loc. cit.*, pp. 435–443.

[5] *Grundriss d. Kolloidchemie*, Chap. I. (T. Steinkopf, Dresden).

light is a variable and important factor. Collecting the various quantities, we have—

Name.	Symbol.	Relation.
Transparency (1)	T	$T = \frac{I}{I_0}$
Transmission-coefficient	a	$I = I_0 a^d$
Absorption-index	k	$I = I_0 e^{-kd}$
Extinction-coefficient	ϵ	$I = I_0 10_1^{-m\epsilon d}$
		$\epsilon = \frac{1}{md} \log \frac{I_0}{I}$
Absorption-ratio	A	$A = \frac{c}{\epsilon}$
or Molecular extinction coefficient	M	$M = \frac{C}{\epsilon}$

where I_0 = intensity *entering* medium.
I = intensity transmitted.
e = base of natural logs.
m = modulus to common logs.
c = concentration in grams per litre.
C = concentration in gm. mols.
d = thickness in cms.

§ 59. The Representation of Absorption Spectra.

Apart from graphic representation of the absorption as judged by the eye, and which is, of course, entirely unreliable for quantitative purposes, misleading even for qualitative ones, there are to be noted the following methods :—

(*a*) Photographic determination of the *limits* of absorption

[1] In the electromagnetic theory of light, for $I = I_0 e^{-kd}$ put $k = \frac{2\pi\chi}{\lambda}$ where λ is the wave-length of light in the given medium. If the thickness $d = \lambda$, we have $I = I_0 e^{-\frac{4\pi\chi}{\lambda}}$ where χ is Cauchy's *extinction index* or Drude's *absorption-index* (cf. Drude, *Lehrbuch d. Optik*, 1900, p. 333).

for varying dilutions till complete transmission is reached.[1] The values of these limits, in terms of the oscillation-frequencies, are plotted against the concentrations or the equivalent thicknesses. Baly[2] has suggested instead the *logarithms* of the concentrations. Such curves give a measure of the *persistence* of a given absorption band. They are termed by Hartley, "curves of molecular vibration," but it must be clearly understood that the actual form and degree of absorption at *any* concentration is not expressed thereby, but the change over a range.

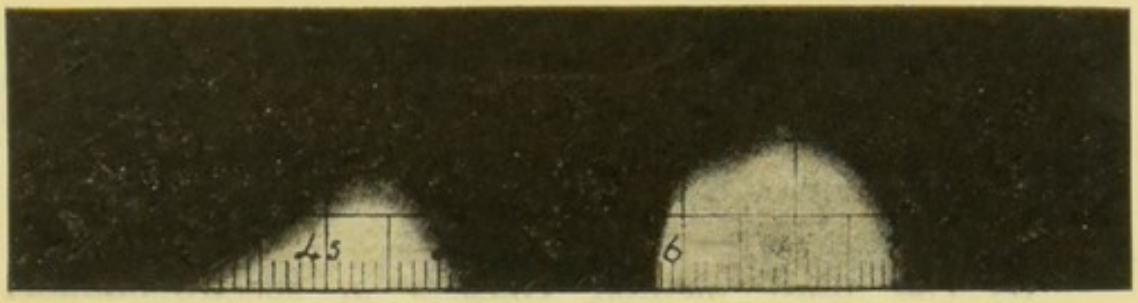


FIG. 25.

(*b*) Instead of photographing the absorption on successive dilutions, the spectrograph may be taken through a wedge-shaped vessel containing the solution, say,[3] when the thickness will vary from zero at the apex to that of the base of the prism. The appearance of the photographed spectra will be clear from the figure (Fig. 25).

Jones and Uhler[4] state that "if the distances from the edge of a positive which is adjacent to the comparison spectrum (which edge therefore corresponds to zero depth in the cell), to arbitrary points on the boundary of a sharply

[1] The method is fully described in E. C. C. Baly's *Spectroscopy*, this series, p. 409. See also W. N. Hartley in Kayser's *Handbuch d. Spektroskopie*, III.

[2] Baly, *loc. cit.*, p. 414; Baly and Desch, *Chem. Soc. Trans.*, **85**, 1039 (1904).

[3] *An Atlas of Absorption Spectra*, by C. E. K. Mees (Longmans, Green & Co., 1909).

[4] *Atlas of Absorption Spectra.* H. S. Uhler and R. W. Wood (Carnegie Institute, Washington, 1907).

defined absorption curve, be called ordinates, and if wave-lengths be considered as abscissæ, we may say that the absorption-constants associated with any two chosen wave-lengths are inversely proportional to the ordinates belonging to these wave-lengths. This statement involves certain assumptions about emission curves and sensibility curves, a discussion of which will not be given here." As a matter of fact, the assumptions involved are, that the emission of the light source and the sensitiveness of the plate are such that light of every wave-length of the light free from absorption would have the same effect, a condition at the best only partially realizable. Undoubtedly, however, the method is the most rapid one for determining the general nature of an absorption band, and for quantitative work where a very high degree of accuracy is not required—as in many applications, etc., of photography—is *ad hoc* satisfactory.

(*c*) The third method consists in spectrophotometric measurement of the intensity quotient $\frac{I}{I_0}$ for a series of wave-lengths (with regard to which see Chap. II., p. 39), and calculation of one of the derived quantities; it is generally most convenient to plot the (Bunsen) extinction-coefficient.

The graphic representation of the extinction as a function both of wave-length and concentration (or mass of absorbing substance) would obviously result in a surface, and it will probably become necessary to consider such surfaces in the future evolution of photo-chemistry.[1]

§ 60. Character of Absorption.

It is quite impossible to deal here in more than a cursory form with the varieties of absorption; for a complete account the reader is referred to H. Kayser's *Handbuch d. Spektroskopie*, Parts III. and IV.

But before dealing with some of the theories as to the

[1] *E.g.* in dealing with the separate effects of intensity and time on photochemical change, cf. Stokes' use of a surface in representing the nature of fluorescence, *Phil. Trans.*, [2] **143**, 479 (1852).

mechanism of light absorption, so important for photochemistry, it is necessary to glance at some of the facts.

Metallic Absorption.—By metallic absorption is understood complete extinction by a thickness of a few wave-lengths of light. For this reason, to simplify calculations, the absorption constants are expressed in terms of the wave-lengths (*vide* footnote, p. 146). In extremely thin layers they show, however, selective absorption.[1] Not only the metals, but certain other substances, such as the aniline dyes, potassium permanganate, and in general, bodies showing surface colour, possess metallic absorption for certain spectral regions.

State of Aggregation.—Generally speaking, bodies in a gaseous state give a more characteristic spectrum than in the liquid or solid condition. The line and band absorption of certain gaseous elements and compounds have been carefully investigated.[2] A remarkable case of the persistence of certain absorption bands with changing condition is that of water, which shows the same absorption bands in the ultra-red in the gaseous, liquid, and solid conditions, and conversely as emission bands in the glowing vapour.[3] The absorption spectrum of benzene vapour [4] is the same as that found for the liquid, save that in the latter the heads of the absorption-bands are shifted some 20 Å. V. toward the red. Probably this is due to the same factor producing shift in solution (see later). The absorption spectra of *ozone* have been studied by Ångström [5] and Hartley,[6] and more recently, for higher concentrations of ozone, by E. Ladenburg and E. Lehmann.[7]

They find that with increased concentration, in addition to bands in the ultra-violet and infra-red, there is a considerable absorption in the red extending further into the visible spectrum as the concentration increases. At the same time

[1] Cf. R. W. Wood, *Physical Optics*, p. 450 (1911).
[2] Cf. E. C. C. Baly, *Spectroscopy*, p. 403.
[3] Paschen, *Wied. Ann.*, **52**, 209 (1894).
[4] L. Grebe, *Zeit. wiss. Phot.*, III. 376 (1905).
[5] Eder's *Jahrb.*, 1905.
[6] *Trans. Chem. Soc.*, **39**, 57 (1881).
[7] *Ann. Phys.*, [4] **21**, 305 (1906).

other bands in the invisible spectrum make their appearance. Liquid ozone gives a strong continuous spectrum in the red and ultra-violet, but probably no bands, certain evanescent strips being attributed to a higher polymer of oxygen.

Changes in the state of aggregation brought about by change of temperature may involve chemical change, when we should expect a marked alteration in the spectrum. In the case of metals and bodies with metallic absorption, the degree of division has a marked influence on the absorption spectrum. This is very noticeable in the colloidal solutions of metals, such as gold, silver, etc., prepared according to Bredig's method,[1] and preparations of these in glass and gelatine.[2] The physical aggregation of the particles, themselves far above molecular dimensions, appears to be a principal factor, though not only the size but also the form and distribution of the secondary aggregates are of chief moment. Like phenomena are shown by certain of the aniline dyes.[3] Siedentopf has observed changes in the absorption of the vapours of the alkali metals, which are not correlated to any change in the molecular weight.[4]

§ 61. Temperature.

In dealing with solutions, the influence of temperature has to be carefully considered.[5] It appears probable that we can distinguish between, (*a*) a physical alteration of the solvent or medium, and (*b*) chemical changes, such as association and dissociation. The influence on spectro-analytical measurements has been studied by G. and H. Krüss,[6] who find that alterations

[1] F. Ehrenhaft, *Drude's Ann.*, **11**, 489 (1903); E. Müller, *Ann. Phys.*, [4] **24**, 1 (1907).

[2] F. Kirschner and R. Zsigmondy, *Drude's Ann.*, **15**, 573 (1904).

[3] S. E. Sheppard, *Proc. Roy. Soc.*, A. **82**, 256 (1909).

[4] See also Dudley, *Ann. Chem. Journ.*, **14**, 185 (1892).

[5] In glasses and crystals the effect of heat has been studied by J. Königsberger and R. A. Houston. In didymium glass the latter found no shift of the maxima of absorption, but in both glasses and crystals there may be relative changes in the intensities.

[6] *Kolorimetrie u. quantit. Spektralanalyse*, 1891, pp. 263–280. They remark on the change of the optical constants of the apparatus with temperature and suggest a mean temperature for measurements of 17·5°.

of temperature always cause displacement of the maxima. Nichols and Spencer [1] constructed isotherms for the absorptions for different wave-lengths of solutions of dyes, which are by no means congruent curves. Similar results were obtained for salt solutions by E. Müller,[2] especially of copper salts. The molecular extinction-coefficient was plotted as a function of the temperature, and the curves varied much for different wave-lengths. Generally, the greater the variation of M, the molecular extinction-coefficient, with concentration, the greater the curvature of the isotherms, but it was not possible to counterbalance the effects of temperature and dilution.

§ 62. Solutions.

The absorption spectra of solutions may be considered in reference to the following points :—

A. The influence of the solvent when one and the same substance is dissolved in various solvents.

B. The influence of concentration.

C. The influence of temperature.

D. The possible reciprocal influence of mixed solutes on each other's absorption.

A. **The Influence of Solvents.**—A. Kundt,[3] from observations on solutions of dyes, stated that the absorption-maxima were displaced to the red in proportion as the refractivity of the solvent increased. This relation which is known as Kundt's law or rule, is by no means confirmed in all cases. H. W. Vogel [4] found numerous exceptions, solvents of greater refractivity not always producing any shift in the absorption. F. Stenger [5] considered that the absorption-spectrum of a solution is only characteristic when the solute is present in its ultimate physical molecules, and that only for such solutions does Kundt's law hold, but he did not define

[1] *Phys. Rev.* (1895), **2**, 344.
[2] *Ann. Phys.*, [4] **21**, 510 (1906).
[3] A. Kundt, *Pogg. Ann.*, 1871–72.
[4] *Monatschr. Berl. Akad.*, 1878, p. 427.
[5] *Wied. Ann.*, **33**, 577 (1888).

quite precisely what was to be understood by this ultimate physical molecule. G. J. Katz[1] made an extended and careful spectro-photometric examination of a large number of dyes in different solvents, preparing the solutions directly. Katz found (*a*) solutions in which the bands remained unchanged in position, (*b*) solutions following Kundt's rule, (*c*) solutions, where one band was displaced, another not, (*d*) cases where change of solvent produced new absorption bands.

Kundt's law has been shown to hold for the cyanines,[2] the isocyanines,[3] certain triphenylmethane dyes, and didymium salts; a physical explanation based on the electron theory will be discussed later. Conditions for its fulfilment appear to be that change of solvent does not favour intramolecular change, or promote association among the solute molecules. Whilst some investigators have suggested that, chemically, an association of the solute with the solvent (solvate theory) is to be assumed as the cause of the phenomenon,[4] others regard the non-existence of any such association as a necessary condition.

Evidence is accumulating at present which points to such a combination between solute and solvent being a necessary condition of solution itself, but whilst the formation of determinate combinations of fixed constitution would perhaps exclude the validity of Kundt's law, the same degree of "solvation" would have no such effect, so that we may, slightly modifying Stenger's criterion, state that Kundt's rule holds if the chemical aggregation of the absorbing molecules is the same in different solvents. It should be pointed out that many dyes form in water, possibly to some extent in other solvents, pseudo or colloid solutions possessing a very modified absorption spectrum.[5] The question of ionization is discussed

[1] *Inaug. Dissertat.*, Erlangen, 1898.

[2] C. Pulfrich, *Wied. Ann.*, **14**, 177 (1881).

[3] S. E. Sheppard, *Trans. Chem. Soc.*, **95**, 15 (1909).

[4] E. Wiedemann, *Wied. Ann.*, **37**, 177 (1889).

[5] Cf. S. E. Sheppard, *loc. cit.*, *Proc. Roy. Soc.*, A. **82**, 256 (1909), and Wo. Ostwald, *Kolloid-chemische Beihefte* II., No. 12, 1911. In the more recent modifications of the theory of solutions, a reconciliation between the ionic and the hydrate theses seems well under way.

in the next section. One may compare the influence of the solvent on absorption with that on the optical rotatory power of dissolved bodies.

§ 63. Beer's Law and Concentration.

B. **The Influence of Concentration.**—The relation between change of concentration and absorption is most important in connection with solutions of electrolytes, generally in water. If ions and molecules possess different absorbing powers, then we must obviously expect considerable changes in the absorption or colour on dilution of conducting solutions. The question has been discussed very completely by G. Rudorf,[1] and Beer's law forms the storm-centre about which discussion has raged, just as Kundt's law does for the action of solvents. We may express this law in the form $\frac{c}{\epsilon} = A$, absorption-ratio, and A is a constant in the ideal case of a disperse system in which no change beyond that of the degree of dispersion occurs on dilution. Then, for electrolytic dissociation, the following conclusions may be drawn[2]:—

(*a*) If the absorption is due to ions alone, then the ratio A should decrease with increasing dilution.

(*b*) If due to undissociated molecules, which give, on dilution, colourless ions, then the absorption-ratio A should increase on dilution.

(*c*) For bodies which do not dissociate, the ratio will be constant (provided no other change, association, etc., occur).

(*d*) If dissociation be so far advanced that dilution has no further influence on it,[3] or if ion and molecule have the same absorption, the ratio will be constant. Hydrolytic dissociation is excluded.

In spite of a considerable bulk of spectrophotometric

[1] G. Rudorf, "Absorption des Lichts in Lösungen vom Standpukt der Dissociations-theorie," *Ahren's Samml.*, **9**, 1904; also *Jahrb. d. Elektronik*, **3**, 423 (1907), *vide* also H. Kayser, *loc. cit.*, p. 148.

[2] Rudorf, *Jahrb. d. Elektron.*, *loc. cit.*, p. 423.

[3] Cf. J. W. Mellor, *Chemical Statics and Dynamics*, this series, Chap. IX., p. 187.

work, reliable data for testing these conclusions are rather scanty. The measurements of Vierordt[1] and Krüss[2] are not, as a rule, suited to its discussion. E. Muller[3] made a careful spectrophotometric investigation of solutions of copper salts, determining the degree of dissociation by conductivity measurements. The relation of the absorption to the dissociation may be expressed thus: Suppose C be the equivalent concentration, *i.e.* in gramme-molecules per c.c. of the solution, and δ the degree of dissociation. The concentration of undissociated molecules is therefore $(1 - \delta)C$, of the ions $C\delta$ (cf. Mellor, *loc. cit.*). If tubes of length d be supposed separately filled with these, then assuming Beer's law for each molecular species we have for a binary electrolyte—

$$I_1 = I\ 10^{-MC(1-\delta)d}$$
$$I_2 = I\ 10^{-N_1C\delta d}$$
$$I_3 = I\ 10^{-N_2C\delta d}$$

hence when all are present together—

$$I' = I\ 10^{-C[M(1-\delta)+(N_1+N_2)\delta]d}$$

or if $N_1 = N_2$

then $m = C\{M(1 - \delta) + 2N\delta\}$

m is the actual molecular extinction coefficient (*vide* p. 146), whilst M may be termed the molecular extinction of the undissociated molecules, N of the ions. If M = N, *i.e.* ion and molecule have the same absorption, Beer's law is fulfilled. This was found to be the case for $CuSO_4$. Hence the colour of the Cu″ ion, probably hydrated, is the same as that of the $CuSO_4$ molecule. If this is not the case, $\frac{m}{M}$ should be a linear function of the degree of dissociation δ. This was not found for any of the copper salts examined; whilst in very dilute solutions of $CuSO_4$, $CuCl_2$, $CuNO_3$, $Cu(CH_3CO.O)_2$ the absorptions are identical,[4] in more concentrated there are

[1] Vierordt, *loc. cit.*, p. 144.

[2] *Loc. cit.*, p. 150.

[3] *Ann. Phys.*, [4] **21**, 518 (1906).

[4] B. E. Moore, *Phys. Zeit.*, **23**, 321 (1906); E. Müller, *Drude's Ann.*, [4] **12**, 76 (1903); P. Vaillant, *Ann. Chim. et Phys.*, **28**, 213 (1903).

divergences. Copper chloride solutions become greenish, with increased absorption in the blue and violet, and this is attributed to the formation of complex ions such as $CuCl_3'$ and $CuCl_4''$, which probably exist in the solid hydrated salt. A dual process of hydration and complex-ion formation appears to occur, so that we have in solution two mutually contradistinctive classes of equilibria, one of which may be termed simplex, or intrinsic, and consisting of adjustment of electrochemical equilibrium *within* the fundamental crystallogenic units of the solution, the *micellae*, as they may be advantageously termed, and in the adjustment of the individual equilibrium of each of which the components, in the sense of the Phase Rule, are probably to be considered proximately as molecular radicles, ultimately as the constituent chemical elements themselves, and, over against those first named, extrinsic or complex equilibria, between the micellae or fundamental solution-units thus composed, and which, in an electric field, will exhibit a relatively free positive or negative surface-charge, according to the inner chemical constitution of the units, and which units, according to the nature of their charge, will, in an electric field, be travelling through the residual neutral matrix engendered by the recombination of micellae of opposite sign. This neutral matrix, being substantially identical with the region of iso-electric strain in the system, may be considered as in equilibrium with a limiting value of the elastic coherence of the system, hence involving the segregation of a solid crystalline phase. The nature of a solution of a copper salt in water, if considered as composed of a *large number* or group of such *micellae*, implies that the solvent, in this case, water, is distributed proportionately amongst the micellae according to the electro-striction exerted by the elemental constituents of the solute, and is partially indicated in the scheme subtended (p. 157). In this no account is taken of the side-issues of defectively solvated oxides and oxy-salts (*e.g.* oxy-chlorides) evolved perhaps by accidental collision and mutual disorganization of the crystallogenic units considered in the partial scheme, and which, occurring often as suspensions of particles in Brownian movement, are familiar to most chemists who

have worked with copper and other metal compounds, and vary immensely according to the nature and strength of the negative radicle. What is here implied is that in a solution of a copper salt in water at ordinary temperatures, the relatively free and independent electric vectors in the system, or, more truly, system of systems, are not elementary ions, but the *micellae* or complex ions. To distinguish such current carriers in liquid solutions from those in gases and flames, where and when the viscosity conditions are remarkably different, it will perhaps be convenient simply to term them electrophores; it is quite possible that the adjustments within the individual *micellae*, as being within a relatively far smaller unit, are, concomitant with the diminution of *range of action* of the forces involved, much akin in nature to those actually obtaining in gases and flames in mass. Not only are solutions at ordinary temperatures more or less impregnated with a dissolved gas-phase, but, as the electric theories of the constitution of matter tend to teach, such a gas-phase is itself only the husk or shell enshrouding the flame of the æther. But, for simplicity, we can regard the adjustments within the *micellae* as independent of the mass-movement of these last, although its concomitant resultant is necessarily allowed for on any theory of solution and electrolysis by considering that the specific mobilities and diffusivities of such electrophores will depend essentially both upon their chemical constitution and molecular weight, and upon the physical state of aggregation of the group. In particular, the mobility of a given electrophore will vary according to the electro-striction of the solvent—*e.g.* water—within the micella—effected by the elemental couple forming its nucleus, though, physically speaking, it would probably be advantageous rather to consider this water-content as an elastic shell of density corresponding to the potential-difference, or electrostatic force of the elementary couple, the solvent being resorbed as *densely* as this force is *tensely* exerted, and the *degree* of its condensation indicated by the *suffix-number* proper to the circular brackets in the scheme appended (p. 157). The excess charge, a surface-charge, of electricity on a given *micella*, can then be considered in either of two ways. Primarily, from

within the *micella*, as the net surplus (positive or negative) of the electrochemical equilibrium conforming the *micella* as an independent unit *sui generis* of the solution, and thus, so to speak, electro-kinetic or voltaic in its origin, or as consequent with the elastic impact of the *micellae*, and as, considered momentarily, an electro-static charge induced by friction. The larger size and coarser grain of the *micellae*, as compared with that of their component molecules and atoms, may be regarded as corresponding to their capacity to resonate principally to the longer waves of the infra-red, whereas resonance in the visible spectrum and for some distance beyond is effected independently of the *micellae* as such, but rather *within* these by the molecules, atoms, and electrons, the intrinsic nature of the responding systems regressing to finer and finer textural modification as the wave-length of the exciting energy diminishes.[1] On the view briefly sketched here, *colour*, in the visible spectrum, probably results from processes independent of the electrolytic dissociation of the solution, processes internal to the solution-units considered as the carriers of the current in electrolysis, and which, although perhaps not crystalline actually in a strict sense are potentially so, or crystallogenic. Each complex cation, for instance, carries concomitantly a tendency to accelerate condensation reactions, it is a catalyst, strictly speaking, in contradistinction to the antagonistic nature of a complex anion of opposite charge. A considerable amount of confusion of thought and misunderstanding is brought about in dealing with chemical dynamics by failure to reflect that acceleration of the velocity of *one* reaction in *one* sense is identically retardation of the velocity of another reaction in the inverse sense thereto.

SCHEME OF SOLUTION-UNITS OF $CuCl_2$.aq.

Cations.	Neutral.	Anions.
$[Cu(H_2O)_4]$: $[CuCl(H_2O)_3]$.	↓ $[CuCl_2(H_2O)_2]$	$[CuCl_4]''$ $[CuCl_3(H_2O)]'$

[1] Some such *continuing* action or after action is evident in phosphorescence.

The stability of a neutral phase or eutectic such as $[CuCl_2(H_2O)_2]$ is, of course, essentially dependent upon conditions of temperature and pressure, but it may be considered as functioning as a membrane semi-permeable to the electrophores.

In the early days of the ionic theory, the coincidence of the colour of different dilute copper solutions was adduced as strong evidence in its favour. Similarly Ostwald[1] showed that all the salts of permanganic acid had identical absorptions at great dilution, which has been confirmed quantitatively by Ewan.[2] The same was found for the salts of rosaniline. But later researches have shown[3] that the permanganates follow Beer's law, consequently ion and molecules possess the same colour, and the *absorption is independent of ionization.* The case of salt solutions has recently been studied by A. Hantsch with various collaborators. For solutions of platinichlorides measurements were made in different solvents and at different concentrations, with Marten's modification of König's spectrophotometer. It was considered that the completely saturated complex $PtCl_6$ would be unaffected by the solvent. Equivalent solutions of the salts and of the acid in the same solvent possess identical absorption. Solvents appear to act in accordance with Kundt's rule, and as with $CuSO_4$, the molecular absorption is independent of ionization.[4] An investigation of solutions of chromic acid and the dichromates[5] showed that the absorptions of equivalent solutions of chromic acid and the dichromates are identical, and that Beer's law is followed to the lowest dilutions. The extinction-coefficients are also practically independent of temperature up to 100°. The table shows values of the molecular extinction-coefficient M for certain wave-lengths for chromic acid and potassium bichromate—

[1] *Zeit. phys. Chem.*, **9**, 579 (1892).

[2] *Phil. Mag.*, [5] **33**, 317 (1892).

[3] P. Vaillant, *loc. cit.*; A. Hantsch and R. H. Clarke, *Zeit. Phys. Chem.*, **63**, 373 (1908).

[4] *Ber.*, **141**, 1216 (1908).

[5] *Zeit. physik. Chem.*, **63**, 373 (1908).

λ	CrO_3	$Cr_2O_7K_2$
405 μμ	324	329
436 μμ	271	288
486 μμ	89	90
546 μμ	1·8	1·7

The chromates also follow Beer's law, but the absorption is quite distinct from that of the dichromates.

Hantsch concludes that (*a*) salts, acids, or bases with completely saturated complexes are optically unchangeable whether ionized or not, no matter what the colourless cation or anion connected with them; (*b*) unsaturated substances, such as anhydrous salts, which may become saturated by the addition of a definite number of water or ammonia molecules forming a saturated coloured complex, change colour by the alteration, but further addition of the combining substance has no further effect, as, for example, in

$$CuSO_4 \rightarrow Cu[NH_3]_4SO_4.$$

Summing up the position as regards ionization and absorption for the inorganic electrolytes considered, it may be said—

Absorption is independent of ionization, and all changes of colour (deviations from Beer's law) on change of concentration are to be attributed to formation or dissociation of complexes, such as hydrates, inner combinations of the solute, as in copper and cobalt salts, or in general to valency changes.[2]

If we turn to the many highly coloured organic bodies the conclusion is the same. Ostwald, in 1893, proposed an Ionic Theory of Indicators. According to this, indicators are weak acids (or bases) the anions (or cations) of which are differently

[1] For similar results with didymium salts, *vide* G. Liveing, *Trans. Camb. Phil. Soc.*, **18**, 298 (1900).

[2] For a general discussion of valency in relation to molecular compounds, see R. Abegg, *Zeitschr. anorg. Chem.*, **39**, 330 (1904), and H. Friend, *Valency* (this series).

coloured from the undissociated acids (or bases). But this unmitigated application of the ionic theory has met similar difficulties to those already reviewed. Phenolphthalein in the solid state is colourless, and also when dissolved in water, but the solid alkali salts are red, whereas we should, on the above theory, expect them to be colourless, like the acid.[1] The phenolphthalein complex must be in a different state in the free acid from that in the alkali salts. Hence it appears that alkalies bring about an intramolecular change, to which the colour is due, and ionization is only secondary.[2] The true acid is similarly coloured to the salts. Similar considerations apply to the case of violuric acid. By careful measurements, in conductivity water free from CO_2, it could be shown that the absorption gave the same degree of dissociation as the conductivity.[3] But violuric acid can exist in two tautomeric forms,[4] and both the conductivity and the absorption are a measure of the intramolecular change, the ionization being only a concomitant. The same result follows from Ewan's spectrophotometric determination of the dissociation of dinitrophenol.[5] Where this intramolecular change is so rapid as to evade perception, solutions of dyes follow Beer's law.[6]

These considerations, whilst militating against any purely "ionic" theory of light absorption, do not affect the validity of determinations of the "strength" of acids, bases, etc., by

[1] The existence of solid solutions, however, makes the supposition that even the solid salts are partially "ionized," a consequent part in the ionic theory of chemical change.

[2] A. Green and King, *Trans. Chem. Soc.*, **89**, 518 (1906).

[3] F. G. Donnan, *Zeit. physik. Chem.*, **19**, 465 (1896); F. Wagner, *ibid.*, **12**, 314 (1892); and Magnanini, *Gazz. Chim. Ital.*, **26**, 92 (1896).

[4] Guinchard, *Ber.*, **32**, 1723 (1899).

[5] *Proc. Roy. Soc.*, **57**, 117 (1894). For tautomerism and intramolecular change in the nitrophenols, see A. Hantsch, *Ber.*, **39**, 1089 (1906).

[6] Salts of para-rosaniline, A. Pflüger, *Drude's Ann.*, [4] **12**, 430 (1903); cyanine in alcohol, Pulfrich, *Wied. Ann.*, **14**, 177 (1881); isocyanine in alcohol and chloroform; S. E. Sheppard, *Trans. Chem. Soc.*, **95**, 16 (1909).

colorimetric or other methods based on light absorption.[1] Only in general, the dissociation-constants determined contain implicitly a constant dependent on the tautomeric change, just as the thermo-dissociation constants of carbonic acid, ammonia, etc., contain an unknown hydration constant.[2]

Examples of such relation are, for example, for a "pseudo-acid"—

$$H.X:O \rightleftarrows X.O.H \rightleftarrows XO' + H'$$

for an ammonium base—

$$X_3N + H_2O \rightleftarrows X_3NH.OH \rightleftarrows X'_3NH' + OH'$$

and the equilibrium relations are correspondingly complex. For the calculation of the "true" ionization constants, see T. S. Moore [3] in a recent paper. E. Baur [4] points out that the fact that different substances, such as $KMnO_4$, $NaMnO_4$, $HMnO_4$, and MnO_4', possess the same spectrum, is difficult to account for, especially in view of the fact that with organic dyes, the replacement of one group by another in the molecule is followed by an alteration in the maximum of absorption of the radicle giving the colour. He suggests that we might speak in this case of optical isomorphism. But deviations of the spectral maxima in organic substances are sometimes very slight. Hartley found in an investigation by the photographic method of the ultra-violet absorption band of the metallic nitrates [5] in aqueous solution that in the case of the nitrates of the heavy metals the band is modified in position, just as when heavy groups are introduced into an organic compound.

Hartley concludes that ionized salts are not entirely

[1] Cf. Friedental, *Zeitchr. Elektrochem.*, **10**, 113 (1904); Salessky, *ibid.*, 203; Salm, *ibid.*, p. 341; and *Zeitschr. phys. Chem.*, **63**, 89 (1908); V. H. Veley, *Trans. Chem. Soc.*, **94**, 652, 2122; J. Stieglitz, *Journ. Amer. Chem. Soc.*, **25**, 1112 (1903).

[2] Cf. v. Zadwidski, *Ber.*, **36**, 3325 (1903); **37**, 153 (1904).

[3] *Trans. Chem. Soc.*, **88**, 1373, 1379 (1907).

[4] *Spektroskopie u. Kolorimetrie* (J. A. Barth, 1906), p. 70.

[5] *Trans. Chem. Soc.*, **81**, 556 (1902), and **83**, 221 (1903).

separated, but that the molecule is so divided on ionization that the movements in the one part are influenced by movements in the other, there being a state of "molecular strain." But before leaving the phenomenal and entering the region of mechanical and other theories of light absorption, it may be pointed out that in solutions of salts, the medium is not the pure solvent, but the solution, and if the absorption of an ionic or other component is modified in accordance with Kundt's law, then we might expect a shift in the absorption bands of salts with the cations of heavy metals owing to the increase in the refractivity of the medium. Hartley found that whilst the nitrates of the metals showed this characteristic absorption band, in the case of the fatty esters of nitric acid, *e.g.* ethyl nitrate, there was no trace of it. From this it might be argued that the ionization was *per se* a sufficient cause for the absorption, contrary to the argument so far enforced. But there is good evidence on chemical grounds that the NO_3 group is in a different condition structurally in the esters, and in the metallic salts, and that it is in this difference and not in ionization alone that the origin of the band absorption must be sought. Or rather, both ionization and colour[1] are separate expressions of the same quality of the molecule. Ionization or capacity for electric conduction (without making any special hypothesis at this stage as to the nature of the ions) and chemical reactivity are known to be intimately related on other grounds, and it appears that the absorption of light, the conduction of electricity, and the chemical reactivity of a substance must all be referred to a common origin. But the capacity for reaction of a chemical individual is expressed conceptually by the structure or configuration of its molecule, and it is evident that we must next proceed to the connection of this with absorption of light.

C. **Influence of Temperature on Solution.**—The conclusions reached with regard to change of concentration may be transferred to the action of heat. Where change of temperature brings about a chemical modification, changes in the absorption spectrum occur, but in chemically stable systems (such as

[1] In this case, invisible colour, or ultra-violet absorption.

the solutions of platinichloride, potassium bichromate, etc.), the alteration is small or nil. Small changes may be referred to the change in refractivity of the medium.[1] Now we have seen that light is to be regarded as a periodic movement, and, as has been pointed out by W. Ostwald[2] and R. Luther[3] the absorption of light by substances implies the persistence in these of preformed periods synchronized to those of the light absorbed. In other words, a spatial discontinuity or corpuscular arrangement in the substance, the discrete particles of which are capable of executing certain movements. The conclusion is the same, of course, as that on which the atomic and molecular theory are based. But if the absorption of light were dependent ultimately on integral, atomic or molecular movements, we should expect a steady and pronounced influence of the temperature. The small temperature coefficient of light-absorption in chemically stable systems points to the conclusion that the preformed periods are dependent on intra-atomic or inframolecular motions, that is, in modern terminology, the movement of electrons, a conclusion to which other lines of reasoning also lead.

The following table, from measurements of G. Krüss, gives an idea of the order of the shift produced by increase of temperature.[4]

POSITION OF MAXIMUM IN SOLUTIONS.

Of	In	At a temperature of				
		20°	40°	60°	70°	80°
Aurine .	Water and trace KOH	534·2	536·1	—	—	538·4
Eosine .	Alcohol .	536·1	—	—	537·2	—
$KMnO_4$.	Water . .	574·9	576·0	—	576·5	576·8
,, .	,, . .	550·9	551·5	—	552·9	553·7

[1] In spectroscopic investigations, possible changes in the optical constants of the apparatus must be borne in mind.

[2] *Lehrb. d. Allgem. Chem.*, Bd. V.

[3] "Die Aufgaben d. Photochemie," *Zeit. wiss. Phot.*, **3**, 265 (1905).

[4] *Kolorimetrie*, etc., p. 263.

The displacements are in both directions, and are of the same order as those produced by change of solvent (*vide* p. 145). Inasmuch as the refractive index of a solution changes with the temperature,[1] the shift must be correlated in part to this. Obviously no conclusions as to change of *intensity* of absorption for a *given* wave-length are of value unless the whole absorption-curve is measured, whenever a displacement of this character occurs.

D. **Mutual Influence of Mixed Solutes on each other's Absorption.**—If the substances do not interact to form a new combination, the light-absorption of a mixed solution will be equal to the sums of the absorptions which the components would exert separately. This additive relation is used for the determination of dyes in each other's presence in solution.[2] Thus let x be the unknown amount, a the known absorption-ratio of one substance in a spectral region; further, y the unknown amount, and b the known absorption-ratio of the other body; finally, E the measured extinction-coefficient of the two substances for the same region. For a second spectral region, let E′ be the extinction, c and d the absorption ratios, and x and y as before the quantities present. Then, assuming Beer's law—

$$\mathrm{E} = \frac{x}{a} + \frac{y}{b}$$

and

$$\mathrm{E}' = \frac{x}{c} + \frac{y}{d}$$

or

$$x = \frac{(\mathrm{E}'d - \mathrm{E}b)}{ad - bc}ac, \; y = \frac{(\mathrm{E}a - \mathrm{E}'c)}{ad - bc}ac$$

For determinations of purpurin and isopurpurin in each other's presence in this manner, see G. and H. Krüss.[3] It must be remembered that in many cases dyes interact, and, especially with certain colloidal dyes, the absorption spectrum of the stable colloid complexes may differ considerably from

[1] Cf. T. Preston, *Theory of Light*, 1895, p. 134.

[2] Cf. also J. Bremer, "Einfluss d. Temperatur gefärbter Lösungen auf die Absorptionsspektra derselben," *Inaug. Dissert. Erlangen*, 1890.

[3] *Spektrokolorimetrie*, 1891, p. 204.

that obtained by summation of the separate solutions.[1] But apart from this, there has been noticed a peculiar displacement of absorption-maxima with pairs of dyes when chemical interaction is out of the question, which is known as *Melde's phenomenon.*[2] The following description from Formanék[3] illustrates its nature. On mixing dilute solutions of methylene-blue and methyl-violet 6B, and determining the principal maxima, it is found that the principal methyl-violet band is displaced toward the red, from λ593·5 to λ595·0. The displacement is greater the greater the proportion of methylene-blue to methyl-violet, whilst with *defect* of methylene-blue the band is displaced in the opposite sense. According to Formanék the same phenomenon takes place if the solutions are not mixed but placed in two cells behind each other. One suspects that an optical deception, due to contrast phenomena, produces this appearance, since in Formanék's method the position of the maximum is determined by eye observation. P. André has shown[4] that when chemical interactions are excluded, the behaviour of summed absorptions is always purely additive.

In the case of gases or vapours, absorptions are sometimes modified in a way which, from ignorance, we must describe as "catalytic." Thus R. W. Wood[5] has noticed an influence on the absorption and fluorescence of mercury vapour, of the presence of air, nitrogen, and hydrogen, as well as chemically active gases such as oxygen and sulphur dioxide. Similarly with anthracene vapour, but here nitrogen and hydrogen do not act. In this connection the fact noted by Hartley,[6] that alcohol vapour inhibits the reversible, photochemically influenced equilibrium of $C_6H_6O_2 \rightleftarrows C_6H_4O_2 + H_2$ in the gaseous state is of interest.

[1] Cf. S. E. Sheppard, *Proc. Roy. Soc.*, A. **82**, 256 (1909).

[2] Melde, *Pogg. Ann.*, **124**, 91 ; **126**, 264 ; Schuster, *Ber.*, **11** (1878) ; G. Krüss, *Ber.*, **15** (1882).

[3] J. Formanék, *Zeitschr. anal. Chem.*, 1900, 424 ; 1901, 520.

[4] "Ueber das Meldesche Phänomen," *Inaug. Dissert.* Bonn, 1907.

[5] *Astrophys. Journ.*, **26**, 4 (1907).

[6] *Trans. Chem. Soc.*, **95**, 52 (1909).

§ 64. Ionization and Absorption of Light.

The explanation of colour and selective absorption of light by chemical systems by the term "ionization" has been somewhat cavalierly treated in the foregoing paragraphs. But the fact is that at present the term "ionization" is used in such a host of conflicting senses, and is itself only a name for a multitude of phenomena suspected to be consequent on a single principle, viz. the distribution of electricity through matter, and which are more or less in need of explanation themselves, that it appears more discrete at present to indicate the undoubted correlation of colour to "ionization," in the sense of capacity for conduction of electricity, without committing ourselves to the view that ionization is the "cause" of colour. The categories of Cause and Effect are somewhat *demodé* at present—one uses them just as one still speaks of the sun rising—but if they are taken as indicating 1 : 1 correspondence in a time-spring, in a sensible interest-process in which they are at the grace of chance, mutually convertible, then it is hardly possible as yet perhaps to assign such an irreducible concomitance to colour and ionization.

Hence, in the ensuing discussion of tautomerism, dynamic isomerism, and of stereo-chemical muta-rotations of structure, the physiological aspects of vision and colour must not be forgotten. It is obviously possible to conceive a very clear and adequate vision of objects in which Colour, other than Black-white, should be entirely absent. In effect, an eye adapted to darkness, that is, actively prepared for penetrating and exploring twilight, tends to see after this fashion, half-tone or *chiar' oscuro* becomes the predominant factor of Form and Movement, and colour-differences are interpreted as nuances of grey.

At present there is in the electron hypothesis the attempt at a theory correlating optical activity (capacity for polarization of light), selective absorption, fluorescence, and structural isomerism of chemical units by the conception of certain enduring muta-rotatory movements in the heart of the chemical

atom, and which movements persist perpetually, although quasi-periodically their velocity-potential, kinetic-potential, or intensity of affinity, passes through absolute minima and absolute maxima.

There are two possible hypotheses at least as to the relation of the atom of an element to its constituent electrons. In the one, following Faraday, we might suppose that each chemical element has but *one* atom—this being the name given to the element's field of influence in space. And accordingly, the quantity usually denominated, "number of atoms of a certain element in a given molecule," would be actually the measure of a definite number of interpenetrations of one atom by another in a certain limited space of time.

However, the alternate version to that which opened itself to Faraday's insight is more convenient to handle, namely, the conception of an indeterminate number of separate minute atoms of the same element, which "atoms" are now, on the electron theory, supposed to be constituted by the interpenetrating spheres of influence or fields of force of a number of mobile electrons.

In the phenomenon of modified absorption noted by Wood, it is very probable that an induced photo-chemical reaction is taking place.

On the solvate theory of the absorption of light by inorganic salts in solution, see recent publications by H. C. Jones.[1] The widening of absorption bands on concentration is attributed to the hydrates becoming simpler and the "absorbers" having freer vibrations. The conception is evidently that the molecule as a whole vibrates, absorbing over a wider range as its mass is lessened. For similar ideas as to the effect of pressure in vapour spectra, see Hartley,[2] who considers, however, that the diffusion of the bands is due to transference of the intramolecular energy to kinetic energy of

[1] H. C. Jones and J. A. Anderson, *Carnegie Publications*, No. 110 (1909); H. C. Jones, on the present state of the solvate theory, *Am. Chem. Journ.*, **41**, 19 (1909).

[2] *Trans. Chem. Soc.*, **95**, 52 (1909).

molecules. But, granted any particular vectors or carriers of *line* absorptions (electrons), increase in the relative motion of these would, by Doppler effects, cause overlap.

§ 65. Absorption and Constitution.

We have seen that in general changes in absorption are correlated to chemical changes. It follows that chemical constitution or structure is determinative for the absorption, whilst conversely, conclusions from the light-absorption can be drawn as to the structure. Light-absorption is in this way a morphological characteristic of chemical species, and the connection is fully treated in another volume of this series.[1] We must, however, touch upon the main empirical and theoretical conclusions. Corresponding to a more advanced theory of constitution, it is among organic bodies that we find the connection furthest worked out, and it was here that the conviction first gained ground that selective absorption was dependent upon certain specific arrangements of the atoms in the molecule. O. N. Witt, in 1876,[2] recognized that colour (in the physiological sense) was conditioned by certain groups or radicles, which he termed *chromophores*, a substance containing a chromophore being a *chromogen*. From investigations on ultra-violet absorption it was apparent that successive introduction of chromophore groups could shift the absorption into the visible spectrum, when the original chromogen was colourless in the ordinary sense. Hence in the widest sense, chromogens are bodies possessing a banded absorption, in the ultra-violet or visible spectrum. It has been shown[3] that bands in the ultra-red are also related to the constitution of substances, yet there is a possibility that the valency relations involved here are of a different order. To this question we

[1] S. Smiles, *Relations between Chemical Constitution and Physical Properties*.

[2] *Ber.*, **9**, 522 (1876).

[3] W. de W. Abney, *Phil. Trans.*, **177**, A. 457 (1886). W. Coblentz.

shall return later. Before instancing any specific chromophore groupings, we must note another term due to Witt.[1] Certain groups, *not themselves chromophores*, when introduced into a molecule already containing a chromophore, may shift the absorption band. This second class of radicles Witt termed *auxochromes*. If the absorption is shifted toward the shorter wave-lengths, the action is termed *hypsochromic*, since the colour is lightened. If toward the red or longer wave-lengths, *bathochromic*, since the colour is deepened, and groups bringing about the respective changes are termed *hypsochromes* or *bathochromes*.[2] As hypsochromic action is rare, the general effect of increase of molecular weight is to deepen the colour.[3] In this terminology, the action of solvents in Kundt's rule is bathochromic, likewise the action of heavy metal cations on the ultra-violet absorption-bands of the nitrate ion (*vide* p. 162).

§ 66. Chromophores and Auxochromes.

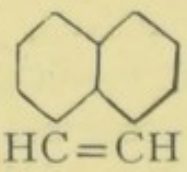
Regarding the benzene C_6H_6 ring as itself a chromogen, specific examples of chromophore groupings are the nitro-group NO_2, especially when repeated as in dinitrobenzene, or supported by hydroxyl OH in the nitrophenols; the azo-group —N=N—, which is the cause of colour in the azo-dyes. These pass into colourless bodies (hydrazo-compounds) on reduction. Again, definite bands have been found by Baly and Desch[4] in the ultra-violet absorption-spectrum of inorganic and aliphatic bodies containing the $—NO_2$ group.

Further, the keto-carbonyl group =C=O, especially when doubled as in benzil—$C_6H_5.CO.CO.C_6H_5$—is an efficient chromophore. The first auxochromes recognized were the hydroxyl group —OH, and the amido group $—NH_2$. Their action is particularly evident when the chromogen into which they are introduced is either colourless to the eye or very

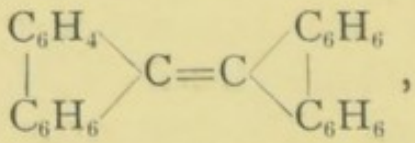
[1] *Ber.*, **21**, 325 (1888).
[2] M. Schutze, *Zeitschr. phys. Chem.*, **9**, 111 (1892).
[3] Nietzki, *Organische Farbstoffe*, 1904.
[4] *Trans. Chem. Soc.*, **82**, 1747 (1908).

slightly coloured. Thus benzo-phenone is colourless, ortho-amino-benzo-phenone, a strong yellow. The $-NH_2$ group generally possesses a more powerful action than the $-OH$ group. Thus p.-nitranilin is deep yellow, p.-nitro-phenol nearly colourless. The arbitrary value assigned to visible coloration must be borne in mind, however. Subsidiary auxochromes are the substituted alkyl-amido, as $-NHCH_3$ and alkyl-oxy groups. It is significant that auxochromic action of the group $N(CH_3)_2$ can be neutralized by making the nitrogen quinquevalent, either by uniting it with an acid or by union with an alkyl-halide.

The chromophore and auxochrome theory of colour has undergone a modification in recent years by which it has lost its original essentially static significance, and to which we may pass by way of the so-called quinonoid theory of colour. With the evolution of the chemistry of dye-stuffs [1] it was found that a large number of dye-stuffs could be assigned a quinonoid structure, and the view was expressed, of which H. E. Armstrong [2] was the chief protagonist, that such a structure, as essentially present in ortho- or paro quinone, is the prime cause of colour. A principal cause of much confusion and delay in arriving at a unitary conception of the relation of light-absorption to chemical constitution has been the arbitrary limitation of the argument to the visible spectrum. Thus benzene, as already stated, has a well-defined series of bands in the ultra-violet. Adverse to the quinonoid theory was the discovery of visibly-coloured hydrocarbons such as the yellow acenaphthylene—



and



the red *di-biphenylene-ethylene.*[3] Another class of coloured hydrocarbons was discovered by Thiele,[4] and termed, on

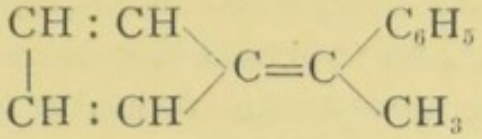
[1] Cf. R. Nietzki, *Chemie d. organ. Farbstoffen* (Berlin, 1906), pp. 21–27.

[2] *Ber.*, **9**, 950 (1876), and in many subsequent publications.

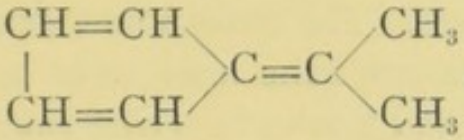
[3] C. Graebe, *Ber.*, **26**, 2354 (1893).

[4] *Ber.*, **33**, 666 (1900).

account of their intense coloration, the *fulvenes*. Such are *methyl-phenyl-fulvene*—



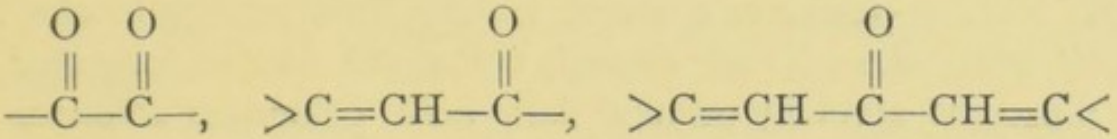
and also bodies not containing a benzene ring, as *dimethyl-fulvene*—



, a yellow oil.

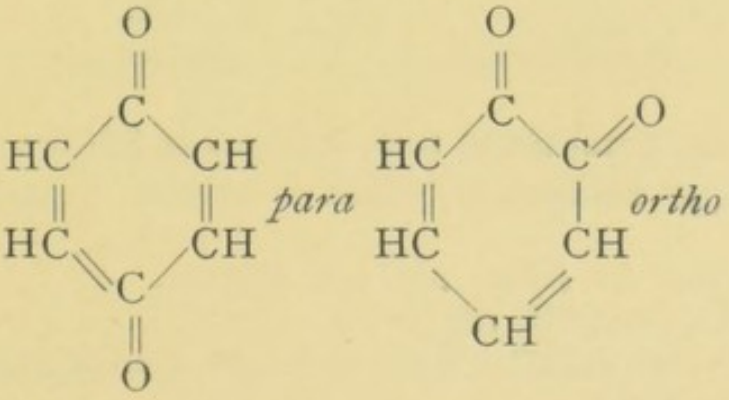
Common to all these is the ethenoid linking —C=C—, which must therefore be pronounced an efficient chromophore. A further difficulty for an exclusively quinonoid theory of colour is furnished by such open chain aliphatic bodies as the *α-diketones*, e.g. *di-acetyl*, $CH_3.CO.CO.CH_3$.

If the chromophore grouping found in the aliphatic substances and the fulvenes are assembled,[1] giving—



and —C=C— repeated, it will be seen that common to them all *is the repeated occurrence of double linkings*. This alone is not sufficient for *visible* colour, but a further condition is that the linkages be closely massed together in the molecule.

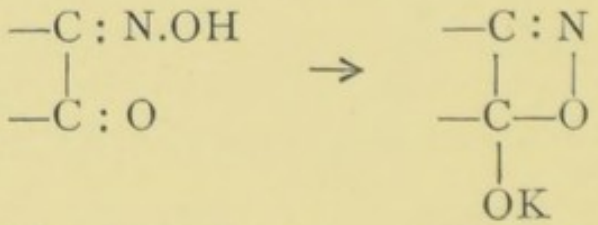
Writing the ortho- and para-benzoquinones in the form—



[1] Cf. R. Haller and H. v. Kostanecki, *Ber.*, **30**, 2947 (1897).

it will be seen that they exhibit a pronounced instance of the foregoing deduction. In agreement with the rule that all chromophore groups contain double bonds is the fact that coloured bodies pass on reduction into colourless.

But even when restricted to aromatic bodies and to the case of visible colour, the quinonoid theory met with difficulties. It was necessary to support it by the idea of atomic rearrangement in the molecule, leading to formulæ capable of quinonoid representation. The quinonoid formula assigned by Armstrong[1] to dioxyterephthalic acid ester was disputed by v. Baeyer,[2] who considered this to be a true benzene derivative. Armstrong considered that when a colourless benzene derivative gave, on change of state of aggregation or on salt formation, a colourless form, that the benzene ring passed into the quinonoid ring by isodynamic change. Like the quinonoid theory itself, this hypothesis has proved extremely fruitful, nor has its scope been limited to benzene derivatives only. Thus, in the purine group,[3] solid *violuric acid* has a feeble yellow tint, its solution in alcohol is colourless, but in water, free from NH_3, it possesses a colour varying from reddish to blue-violet, whilst the salts are strongly coloured. Hartley obtained by means of specially purified water quite colourless solutions which become coloured with alkali, which is due to an isodynamic change in part of the molecule—



imininoketone. coloured salt.

Hantsch[4] has generalized such changes as follows: if a colourless hydrogen compound, which is soluble in water, manifest

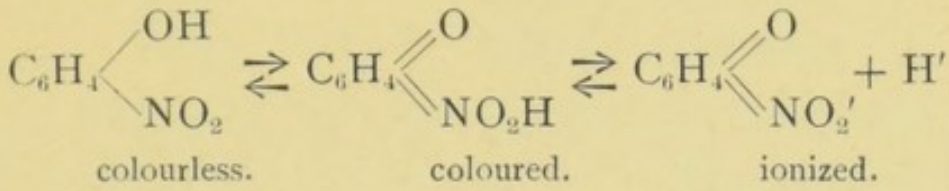
[1] *Proc. Chem. Soc.* (1892), 103, 143, 189, 194.

[2] *Ann. d. Chemie*, **245**, 189 (1880).

[3] Cf. W. N. Hartley, *Trans. Chem. Soc.*, **87**, 1796 (1905); J. Guinchard, *Ber.*, **32**, 1723 (1899).

[4] *Ber.*, **32**, 575 (1899).

coloured ions and alkali salts, the substance is a pseudo-acid, which on salt formation gives derivatives of the true (unstable) acid form. In a similar manner, pseudo-bases may exist colourless, but giving coloured salts with acids.[1] This conception of the nature of the change from a colourless to a coloured condition has been applied by Hantsch to various specific problems of structure in organic chemistry, as, for example, with regard to the triphenylmethane dyes,[2] and also the nitrophenols,[3] for which the following transmutation is conceived—



Hantsch's theory has been disputed by Kaufmann,[4] who argues from the auxochrome theory that the formation of coloured from colourless bodies on salt formation does not necessarily imply a change of structure, in that salt formation may simply shift a band in the ultra-violet into the visible spectrum.

The issue between the chromophore *cum* auxochrome theory and Hantsch's idea of a definite change of structure as the cause of visible colour can be decided in most cases by appeal to the spectrograph. In certain cases it is obscured by quibbles as to whether a particular solution is visibly coloured or not;[5] here it should be remembered that Spring has shown[6] that many so-called colourless liquids show a tint when viewed in sufficient depth. Kaufmann's main contention, that the introduction of certain groups can push an

[1] On pseudo-acids, see H. Euler, *Ber.*, **39**, 1607 (1906), and A. Hantsch, *ibid.*, **39**, 2068 (1906).

[2] *Ber.*, **33**, 278 (1900).

[3] *Ibid.*, **39**, 1073, 1084 (1906).

[4] *Ibid.*, **39**, 1959 (1906).

[5] Cf. *Annual Reports on the Progress of Chemistry, Chem. Soc.*, 1907. *Sec. Organic Chemistry*, p. 147.

[6] *Arch. d. sc. phys. et nat.*, [4] **2**, 105.

ultra-violet band over the colour-threshold, is *à priori* indisputable. Many cases of the shifting of a band toward the red end of the spectrum have been given by Hartley, the shift being greater the higher the molecular weight of the group introduced. The effect of chlorine substitution into the pyridine molecule will serve to exemplify this. Baker and Baly[1] give for the oscillation-frequencies of the heads of the absorption bands of three chlorinated pyridines the following values :—

Trichloropyridine	3650
Tetrachloropyridine	3500
Pentachloropyridine	3400

As a criterion, we may assume that simple displacement of a band does not involve a change of structure in the ordinary sense. An essential change of structure correlated to band absorption would involve the production of a new band.

None the less, Hantsch has demonstrated the elasticity of his theory in many specific instances. With regard to the two chief auxochromes, $—NH_2$ and —OH, the inclusion of these in the molecule so increases the possible graphic formulæ that can be written for it, that the difference between the two views does not amount to much. The difference is largely one of point of view. On Hantsch's theory, colour is a function of certain structures in the molecule, considered as wholes, and the view may be described as unitary. Kaufmann's is so far dualistic that a *potential* colour structure is developed by the presence of auxochromes. The mere shifting of absorption bands by substitution does not necessitate any dualistic conception,[2] but the two prime auxochromes, $—NH_2$ and —OH, lead to far-reaching modifications in the chemical behaviour of the molecule. So that Kaufmann's theory of auxochromes becomes largely a special analysis of the general physico-chemical properties of the amine $—NH_2$ and the hydroxyl —OH group. That no absolute contrast of function can be assigned to auxochrome

[1] *Chem. Soc. Trans.*

[2] Such as developed by J. Schmiedlin, *C.R.*, **139**, 872 (1904).

and chromophore is allowed by Kaufmann himself.[1] For a complete exposition of Kaufmann's views, his monograph on the auxochromes[2] should be consulted. Actually the unitary structure view of Hantsch (comprehending the notion of intramolecular rearrangement and the quinonoid theory) and the theory of Kaufmann are tending to merge. This synthesis is being brought about by the counterpoising of static conceptions by kinetic ones, by the recognition of the essentially dynamic nature of light-absorption, and of the protean character of the absorbing molecule.[3]

§ 67. Chemico-dynamic Theories.

The theories touched upon in the foregoing are essentially static and formal. Certain configurations are found to be associated with colour, or more generally, with selective absorption, but no explanation as to how this is brought about is involved. The relation of isodynamic change to colour involved in the theories of Hantsch and Armstrong is only that of an unspecified path leading from the uncoloured to the coloured form. But the constant connection of isodynamic change or dynamic isomerism[4] with colour—it may be said

[1] *Die Auxochrome*, p. 22.

[2] *Die Auxochrome*, *Ahrens Sammlung*, XII., 1907.

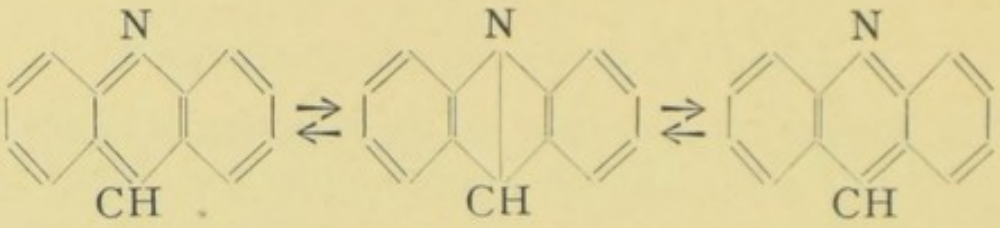
[3] The relation of absorption, refractivity, etc., to chemical structure, is dealt with more fully in Dr. Smiles' *Physical Properties and Chemical Constitution*, this series.

[4] Dynamic isomerism is the most general term denoting the condition of substances to which from their reactions more than one graphic formula can be assigned, *i.e.* they behave now according to one, now according to another. In solution the equivalent forms are believed to exist in equilibrium, transition being readily influenced by solvents, catalysts, etc. The term "tautomerism" is often used in the same sense, but was historically applied (van Laar) to the enol-keto equivalence—

$$\begin{array}{ccc} -C.OH & & -C{=}O \\ \| & \rightleftarrows & | \\ -CH & & -CH_2 \end{array}$$

in which the wandering of a hydrogen atom is involved. The term "desmotropy" (Jacobsen) is also used for tautomery. Cf. T. M. Lowry, *B. A. Report on Dynamic Isomerism*, 1904

that no organic substance shows an absorption band unless a possibility of a tautomerism exists within the molecule—imposes the conviction that the connection is causal, as was suggested by Lowry.[1] That *emission* of light as manifest in the fluorescence of organic substances is due to tautomerism, was suggested by J. T. Hewitt.[2] Thus the fluorescence of acridine was attributed to internal vibrations in the molecule conditioned by symmetric double tautomerism, the molecules oscillating between the extreme positions schematically indicated as follows :—



That some kind of molecular vibration was responsible for selective absorption was fully recognized by Hartley and other workers in the field of absorption spectra, but the nature of the vibrations was not precisely conceived. In 1904, Baly and Desch[3] investigated by Hartley's method (*vide* p. 147) the ultra-violet absorption of ethyl acetoacetate and acetyl acetone, both tautomeric bodies containing a labile hydrogen atom, and of their metallic derivatives. It was found that *neither of the possible modifications* when in a pure state gave an absorption band, but that when the two are present in equilibrium with one another, a very decided band is developed. Further, it was found that the oscillation-frequency of the light-waves absorbed is nearly the same for all the substances examined, whether those containing a hydrogen, glucinum, sodium, or even a thorium atom, in the so-called labile condition. In a subsequent paper[4] these results were confirmed for a large number of other enol-keto tautomerides and their metallic derivatives. The writers point out that some vibration or free

[1] *Loc. cit.*, *B. A. Report on Dynamic Isomerism*, 1904.
[2] *Zeit. phys. Chem.*, **34**, 1 (1900).
[3] *Trans. Chem. Soc.*, **85**, 1029 (1904).
[4] *Ibid.*, **88**, 766 (1905).

period, synchronous with that of the light-waves absorbed, must exist in the system, and that this must be conditioned by the tautomeric process itself. It cannot, however, be a vibration of the labile atom, for not only does the frequency of the band bear little relation to the mass of the mobile atom, but it is itself of a different order, of far greater frequency than that of the motions usually attributed to atoms. They attribute it, therefore, to the change of linking expressed in the equation—

$$-CH_2.CO- \rightleftarrows -CH : C(OH)-$$

During the wandering of the hydrogen atom we may conceive of an intermediate transition phase—

$$-CH.C-$$
$$\quad\quad\;|$$
$$\quad\quad HO$$

during the momentary existence of which the two carbon atoms and the oxygen atom are actually changing their valency-condition or linking, and they assign the absorption band to this transition.

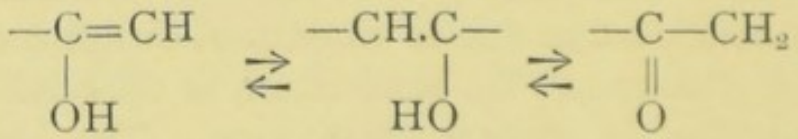
A physical meaning to this change of valency is obtained by consideration of the electron theory. On this theory each atom is a system of small corpuscles or electrons, in continual motion round a common centre, and the emission spectra of gases are conceived as due to vibrational disturbances of these systems of electrons. We shall return to the consideration of this conception in greater detail later. The electrons are elementary electrical quantities, whereof we shall assume for the nonce that only one kind, negative electrons, exist.[1] Chemical affinity may be conceived as due to electric attract tion, to which a mechanical meaning may be attached by assuming Faraday tubes of force between the atoms, each tube representing the line of passage of one electron from one atom to another, and at the same time, the chemist's single bond.[2] A rearrangement of these tubes or linkings will cause a disturbance in the vibrations of the systems of electrons, whereby

[1] Cf. p. 166, and Sir W. Ramsay, *Electron as an Element*, *Trans. Chem. Soc.*, **93**, 778 (1908).

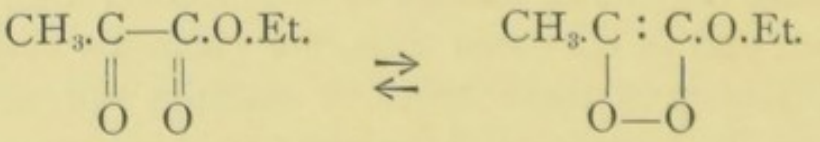
[2] Baly and Desch, *Trans. Chem. Soc.*, **88**, 768 (1903).

light of correlated period will be absorbed in accordance with the theory of resonance dealt with later.

Without further specializing the electronic conception of valency, we will consider some further consequences and developments of Baly's theory. Assuming the band to be due to the tautomeric process, then the degree of absorption or persistence of the band will be a measure of the number of molecules in the transition or oscillating state at any moment. Further, the oscillation-frequency of the band for the same type of valency-change will be the same approximately, whatever the molecule in which it takes place, but we may expect an increase in the mass of the molecule to damp the vibrations, *i.e.* lessen the frequency of the band and so shift it toward the red, for the period of the vibration of the electrons will depend upon the mass of matter in their immediate neighbourhood. In this way the *bathochromic* influence of substituents (*vide* p. 168) is physically explainable. In conjunction with various collaborators, Baly has extended the application of this conception to other cases of ultra-violet (and implicitly) visible absorption bands. Thus the idea of a "nascent" carbonyl group implied in the transition phase of the enol-keto transmutation—



is used to explain the absorption and reaction properties of bodies containing carbonyl groups, but not undergoing tautomerism in the sense of the wandering of a hydrogen atom,[1] such as ethyl pyruvate, for example, which may be supposed to be, during absorption, oscillating before the forms—



Baly and Stewart point out that it is difficult to represent such

[1] E. C. C. Baly and A. W. Stewart, *Trans. Chem. Soc.*, **89**, 489, 502, 514 (1906).

processes by the usual structural formula which only indicates a static condition of the molecule, whereas the process of diathesis considered is essentially kinetic. For such an oscillation between the residual affinities of contiguous atoms they propose the term *isorropesis*.

The yellow colour (due to a band in the violet) of the α-diketones and of the quinones is attributed to isorropesis between the residual affinities of the oxygen atoms. It is pointed out that the assumption that two compounds must be fundamentally different in constitution if one is coloured, the other not, is not trustworthy. For, as will be shown directly, on this view colour (or absorption) is an evidence of the dynamic state of the molecule, and the disturbing influence necessary to start the oscillation between residual affinities may be lacking.

Each type of isorropesis (or potential tautomerism[1]) is correlated to its own absorption band. Thus the isorropesis of the oxygen atoms of the quinones furnishes one absorption band, whilst in the case of the nitroanilines and the nitrophenols it is shown[2] that oscillation between two nitrogen atoms in the one case and an oxygen and nitrogen atom in the other may be assumed to explain the colour.

It is outside our province to discuss particular applications of the isorropesis theory to problems in constitution and reaction chemistry. For this the reader is referred to the numerous papers of Baly and his collaborators in the *Transactions of the Chemical Society*, 1905 *et seq.*, and to the volume on *Physical Properties and Chemical Constitution* in this series by Dr. S. Smiles. The dynamical theory of the chemical molecule is, however, of such vital importance for photochemistry that we must consider it in relation to three problems, viz. the constitution of the benzene molecule, the nature of ionization and chemical reactivity, and to so-called photo-chemical extinction.

[1] The tautomerism is actual in the case where a labile hydrogen atom exists.

[2] Baly and Stewart, *loc. cit.*, p. 514.

§ 68. The Benzene Molecule.

Apart from its general chemical importance, benzene and benzene derivatives figure largely in the list of photo-chemically important substances. Benzene shows in solution or as vapour seven absorption bands in the ultra-violet.[1] Baly and Collie account for these by the assumption that the benzene molecule is in a state of pulsation or vibration, there being a continuous rearrangement of the linkages between the carbon atoms. Applying the idea of isorropesis as invented for the aliphatic tautomerides, and assuming that an even number of carbon atoms is concerned in each individual process, we can differentiate between the transition phases in which any two, four, or all six of the carbon atoms are concerned.

This gives *seven* and only seven forms or possible conditions of making and breaking of linkages, and to these the seven absorption bands are referred.

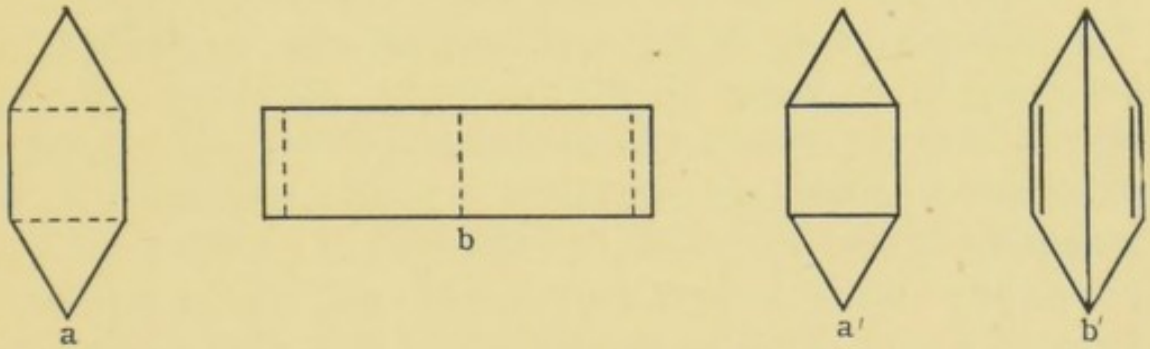
That some such internal motion exists in the benzene molecule was suggested by Kekulé in 1865 as the reason why no isomeric ortho bodies were obtainable according as the contiguous substituted groups are united by a double or a single linking. The vibration theory was strongly advocated by Collie[2] as the only solution compatible with the protean reactivity of the benzene molecule. Internal vibration through a succession of isodynamic phases is also considered by Hartley[3] to be the cause of the absorption of light by benzene. Hartley, however, only considers six changes of phase, the alteration between double and single linkings passing by a

[1] E. C. C. Baly and J. N. Collie, *Trans. Chem. Soc.*, **87**, 1332 (1905); Hartley and Huntingdon (*Phil. Trans.*, **70**, 257 (1879) gave seven bands; later Hartley and Dobbie (*Trans. Chem. Soc.*, **73**, 695 (1898)) six. Friederichs gave for benzene vapour (*Zeit. wiss. Phot.*, **3**, 154 (1905)) eight bands, whilst Grebe (*ibid.*, **3**, 379 (1905)) gives seven, but considers that the one at 2633 Å.U. (which would correspond to Baly and Collie's band at 2658 Å.U., all the bands being displaced in solution by 25 Å.U.) is due to an impurity, which in view of Baly and Collie's results seems doubtful.

[2] *Trans. Chem. Soc.*, **71**, 1013 (1897).

[3] *Ibid.*, **88**, 1822 (1905).

vibratory motion regularly from the first to the sixth position clockwise. The changes in the linkages of the contiguous C-atoms give six alternate modes of motion in all. Hartley likens these to a number of alternate compressions and extensions of an elastic ring at six different points, which may be supposed to act upon the ether. As was stated, Baly and Collie do not consider it possible to conceive of any sufficiently definite differences between the linkage changes around the six atoms taken individually to justify the assumption of a separate absorption band for each. The views of Baly and Collie and of Hartley are not, however, irreconcilable, the difference appearing to be chiefly in the *locus* assigned to the absorption, the former attributing this essentially to the *process* of linkage change, whilst Hartley's eye is fixed on the individual carbon atoms. The phases through which the molecule is conceived to pass are substantially the same, being the vibrations of an elastic ring pulsating between two displaced forms.



Each carbon atom has a residual affinity, which, in the limiting phase *a* or *b* result in the formation of linkings shown by the dotted lines.[1]

So far as the absorption of radiant energy is concerned, any such conceptions are only an approximate and sketchy analysis of the vibrations involved, which are certainly of a very complex character. Thus observations of the absorption

[1] For fuller details and applications to particular reactions, see Baly and Collie, *loc. cit.*, and Baly, Edwards, and Stewart, *Trans. Chem. Soc.*, **89**, 525 (1906), and for a complete discussion of the stereochemical formulæ for benzene, A. W. Stewart, *Stereochemistry*, this series, p. 502.

bands in benzene vapour show that the main bands referred to above are really *groups* of bands, with their maxima towards the red, shading off to the shorter wave-lengths.[1]

The limitations imposed by the theory of undivided valencies and by the static representations of molecular structure have led Kaufmann [2] to adopt a dynamic conception of the benzene molecule. The benzene nucleus is considered as being present in different conditions from substance to substance, out of the multitude of which only the *limiting* conditions can be represented by our ordinary static formulæ, the intermediate ones only by the application of Thiele's theory of partial valencies.[3] Auxochromes favour the limiting state expressed by Dewar's form, (*b* of Baly and Collie), which Kaufmann terms the D-condition, which is, however, one of kinetic, not static, stability. In it the benzene ring is distinguished by maximal luminescent power and maximal magneto-optical anomaly. What may be termed the dynamic theory of the molecule, as here exemplified in benzene, is a view to which many phenomena point, especially in connection with optical properties. The number of substances which are recognized to be in a state of dynamic isomerism is ever increasing, and although at present these are principally organic bodies, there is also evidence that a similar state of affairs must be recognized for inorganic substances. The conception that the configuration is not fixed and immutable was expressed by Divers.

It is necessary to be cautious in assuming that the static or graphic formulæ assigned to compounds from their reactions ever represent more than a momentary phase of the molecule. *For the configuration may be determined by the reaction itself.* This reasoning by no means implies that the molecule is a formless flux, but that, to borrow a term from the psychologists, it has a multiple personality. In some cases, two sharply

[1] Cf. Friederichs, *loc. cit.*, *Zeit. wiss. Phot.*, 3, 154 (1905).

[2] H. Kaufmann, *Die Auxochrome*, pp. 73 *et seq.*

[3] Cf. H. Freund, *Valency*. This series.

separated personalities pertain to the same individual.[1] By means of a certain reaction, we obtain, so to speak, an instantaneous photograph of one of the possible phases.

Certain phenomena in the allotropy of the elements point to similar isodynamic conditions existing here. This appears to be the case with the two liquid modifications of sulphur,[2] both of which have the same molecular weight, S_8. It is significant that this equilibrium is displaced by light (*vide* 233).

§ 69. Isorropesis and Ionization.

Hartley, from the observation that the ultra-violet band of solutions of metallic nitrates is shifted toward the red by heavy metal cations concluded that there must be an intimate connection between the metallic atom and the NO_3 group even in completely ionized solutions. Baly and Desch[3] support this view, considering that in electrolytically dissociated solutions the bond between the two ions is not destroyed, but that the solvent by its residual affinity for the ions merely tends to draw them apart. When the two ions are sufficiently separated to allow a free interchange of electrons between different molecules, we have the condition called ionization, which is partial or more or less complete according to the number of interchanges per unit time. If the separation of ions has not reached the critical distance no interchange takes place. It is suggested that in aliphatic tautomerides the substances may be regarded as only sufficiently dissociated in solution to allow of interchanges between different parts of the same molecule—the specific reactivity being as it were short circuited.

The labile atom is thus in a state of incipient dissociation, and may be termed a potential ion. On this view the persistence of the band in tautomeric substances is a measure of the extent to which the labile atoms are separated from the rest of the molecule. Baly and Desch find support for this

[1] As a figure of speech, one might speak of the molecule in the static, non-reactive condition as asleep ; in the kinetic condition, as awake.

[2] Cf. A. Wigand, *Zeit. phys. Chem.*, **63**, 273 (1908) ; H. Kruyt, *ibid.*, **64**, 513 (1908).

[3] *Loc. cit.*, p. 770.

in the fact that the persistence is increased by alkali, whereby a maximum is reached, the amount of alkali being greatly in excess of that necessary to convert the whole substance into the sodium derivatives. This maximum persistence corresponds to the condition that the separation of all the labile atoms from the rest of the molecule has overstepped the critical value, and that perfectly free interchanges are taking place. In agreement with this view is the fact that the sodium derivative of ethyl acetoacetate is ionized and hydrolyzed, the aluminium derivative but very little.

The process of dissociation is thus conceived as continuous, isorropesis is potential tautomerism, tautomerism potential ionization, and the action of the solvent is continuous. Light absorption, chemical reactivity, and ionization appear as correlated manifestations of mobile electrons.

Reference may be made here to von Baeyer's theory of *halochromy* as illustrating the difficulties of correlating static configurations to colour. To indicate a distinction between ionizable and non-ionizable valency, Baeyer[1] proposed in certain cases the use of wavy line. Phenomena where this would be used are such as where colourless or weakly coloured bodies unite with acids to form coloured salts, but it is not possible to attribute this to the formation of a new chromophore, such as the quinonoid configuration. Such halochromy is met in several ketones containing the grouping—

$$-C{=}HCH-CO-CH{=}CH-$$

thus dibenzoyl-acetone, which is yellow, forms a red compound with dry HCl. The red solution of triphenyl-carbinol in concentrated sulphuric acid is another instance. Most structure theories assume tetravalent oxygen in these cases.

§ 70. Infra-red Absorptions and Harmonics.

The more important references are given in the footnote. It has already been stated that the ultra-violet bands of benzene

[1] Baeyer and Villiger, *Ber.*, **35**, 1189 (1902). Cf. also K. Gebhard, *Journ. prakt. Chem.*, **84**, 361 (1911).

and its derivatives show themselves, on greater dispersion, to be groups of finer bands or lines, channelled or fluted spectra. According to Grebe [1] the heads of the ultra-violet bands in benzene vapour are—

λ ·2689 μ, ·2676, ·2665, ·2587, ·2526, ·2463, ·2412, ·2360.

In liquid benzene they are displaced some ·0015 μ. Coblentz finds in the ultra-red some seven to eight bands, which are also fluted. These are at—

13 μ, 11·8 μ, 9·8–10·3 μ, 8·78 μ, 6·75 μ, 6·25 μ,[2] 5·4 μ, 3·25 μ.

It is probable that some relation exists between these ultra-red and the ultra-violet bands, such as certainly exists among the infra-red ones themselves. In the case of open-chain hydrocarbons, the absorption bands appear to form a simple harmonic series in certain cases, there being, for example, bands at—

·85 μ, 1·67–1·72 μ, 3·25–3·43 μ, 6·75–6·86 μ, and 13·6–14 μ,

corresponding to —CH_2 groups.

It should be remarked that Schutze [3] and Krüss [4] state that some sort of harmonic relation exists between the ultra-violet and the infra-red bands for organic dye-stuffs.

A very important series of infra-red bands are those of *water*, lying at [5]—

·77 μ, 1 μ, 1·25 μ, 1·50 μ, 1·95 μ, 2·05 μ, 3·06 μ, 4·7 μ, and 6·1 μ.

Ammonia (NH_3) shows numerous deep bands between 9 μ to 13 μ; O_2, faint bands at 3·2 μ and 4·7 μ; N_2 and H_2 no bands.

These infra-red bands will probably be found of great importance for the theory of solutions, since it is likely that by them energy of low frequency is reconverted into energy of high frequency, and that to this reformation of high frequency vibration is due the "ionizing" power of solvents.[6]

[1] *Zeit. wiss. Phot.*, **3**, 376 (1905).

[2] Weak in benzene, strong in derivatives.

[3] Schütze, *Zeit. phys. Chem.*, **9**, 109 (1892).

[4] P. Krüss, *ibid.*, **51**, 257 (1905).

[5] Paschen, *Wied. Ann.*, **52**, 209 (1894).

[6] Generally on infra-red absorption, see Abney and Festing, *Phil. Trans.*, **172**, 887 (1882), and in particular, W. Coblentz, *Jahrb. d. Rädioaktiv.* **4**, 7 (1907).

The infra-red bands on this view correspond to the associated, condensed, or polymerized states of the substance, which on absorption of radiation of low frequency syntonic with the heavily damped pulsations in the condensed states of matter, tend to dissociate slightly, the end result through the chain being a slight emission of high frequency energy, found as "ionization" if another conductor is present.[1]

§ 71. Isorropesis and Photo-chemical Extinction.

We have already referred to what is known as Draper's absorption-law for photo-chemical reactions, viz. that only the light absorbed is chemically active. On the other hand, the converse of this, which would be that every substance absorbing light is light-sensitive, that is, undergoes chemical change, does not appear to hold.[2] In addition, even in a light-sensitive substance, not all the rays absorbed are active in promoting overt chemical change. Pure aqueous solutions of inorganic copper-salts, such as $CuSO_4$, which have a powerful absorption in the yellow and red, are not chemically altered thereby.[3] Again, alkaline copper tartrate (Fehling's) solutions have a powerful absorption in the red and yellow, extending into the infra-red. This absorption appears to cause no chemical change. But in addition there is an ultra-violet absorption which leads to chemical decomposition and to the deposition of cuprous oxide Cu_2O. Bichromate salts which absorb blue, violet, and ultra-violet rays, are stable by themselves in light, but in the presence of organic substances the bichromate is reduced, the light absorbed now being active.[4]

[1] Cf. H. Armstrong, *Science Progress*, **3**, 638 (1909). Also it must be remarked that from recent work of T. M. Lowry and C. Desch, it appears that even in the case of isodynamic chemical changes the presence of a *catalyst* is necessary (*Chem. Soc. Trans.*, **108**, 751 (1909)).

[2] Cf. J. M. Eder, *Hdbuch. d. Phot.*, vol. i. p. 13.

[3] It should be noted that Hartley (*Trans. Chem. Soc.*, **81**, 556 (1902)) has remarked slow changes in solutions of pure salts not usually considered light sensitive, and that similar observations were made by Kohlrausch.

[4] Cf. J. M. Eder, *Hdbuch. d. Phot.*, II., 13 (1906).

We are, however, dealing here with complex reactions and systems from which we cannot expect to deduce simple relations. It is feasible that in these cases it is the tartrate molecule and the organic substance (gelatine, etc.) which are specifically sensitive to electric rays, and which "sensitize" the copper salt and the bichromate respectively, *i.e. after* change by light, react with them chemically. The question arises, does a system which is undergoing chemical change in light absorb light differently from the reacting substances themselves? Bunsen and Roscoe considered that it does. They measured the absorption of light by chlorine and hydrogen separately, and then when reacting in light to form HCl, and found the latter absorption greater.[1] They concluded that there was an absorption by the reaction itself, which they termed "photo-chemical extinction," over and above the ordinary absorption of the components, which they called "optical."[2] Various objections have been raised to this division. Pringsheim[3] pointed out that it was not demonstrated that the proportion of radiation which in pure chlorine only heated it, did the same in the reacting mixture. Given the possibility of chemical action, a larger portion of energy might be used for activating or altering the condition of the chlorine so that it reacted to form HCl. Lemoine[4] attempted a similar experiment for the decomposition of ferric oxalate, but concluded that the "chemical extinction could not be more than 1 in 10,000 of the total."

It would be very desirable to have similar measurements in the case of a reversible photo-chemical reaction of the first type. Unfortunately, only one such reaction in homogeneous solution has been investigated, viz. the conversion of anthracene into dianthracene by light,[5] which is reversible in that in the dark the dianthracene reverts spontaneously to anthracene,

[1] *Pogg. Ann.*, **101**, 254 (1855); Ostwald's *Klassiker*, **38**, 20.

[2] Eder proposed the terms "photo-thermal" and "photo-chemical" for absorption, according as the energy is transformed into heat or chemical action.

[3] *Wied. Ann.*, **32**, 384 (1887).

[4] *C. R.*, **118**, 525 (1894).

[5] R. Luther and Fr. Weigert, *Zeit. phys. Chem.*

and very few extinction-measurements are to hand for this. In considering the possibility of reaction-absorption in such a case, we must examine the dynamics of the reaction, especially the equilibrium. Luther and Weigert found (see *infra*, p. 214) that to any light-intensity there corresponds a given concentration of dianthracene. This equilibrium value is only a stationary condition, since on removal of light the dianthracene depolymerizes. Luther[1] compares such a case to the maintenance of a water-jet, which is kept to a certain height only by continuous supply of energy from without. Or one may compare it with the level of water in a bath with both outlet and inlet taps turned on. Such stationary conditions are not peculiar to photo-chemistry, since a similar condition occurs in electrolytic decomposition, where the products are not removed.[2] Luther, however, contrasts this state, an essentially *dynamic* equilibrium, with an ordinary chemical equilibrium, on the ground that the latter is *static*. It is questionable if this position is tenable. A chemical equilibrium, such as $NH_3 + HCl \lesseqgtr NH_4Cl$ is *dynamic*, either from the kinetic-molecular view[3] or from the thermodynamic view, and there seems no reason to assert a capital difference between reactions typified by

$$(a)\ A + \text{light} \rightleftarrows B$$
$$(b)\ A_1'' + \text{electricity} \rightleftarrows B_1$$
$$(c)\ A_2'' + \text{heat} \rightleftarrows B_2$$

save that, in the sense of the Phase Rule, there is one more inner variable (besides temperature and pressure) in the first two cases.

None the less, the distinction between optical and chemical extinction has been generally accepted,[4] and related to it the conception has arisen of two different classes of photo-chemical reactions, one in which light performs work against chemical

[1] R. Luther, "Die Aufgaben d. Photochemie," *Zeit. wiss. Phot.*, **3**, 260 (1905).

[2] Cf. Salomon, *Zeit. phys. Chem.*, **24**, 54 (1897).

[3] Guldberg and Waage, *Études sur les affinités chemiques*, 1867.

[4] See J. M. Eder, *loc. cit.*; W. Nernst, *Theoretische Chemie*, 4th edit., p. 721.

forces, equivalent to the chemical extinction, the other in which its action is catalytic.[1] In the former, light is supposed to bring about reactions not otherwise occurring, in the latter to accelerate a "slow" dark reaction. We shall have occasion to discuss this distinction again, here it need only be remarked that the so-called catalytic light-reactions are probably due to the superposition or coupling of a non-photo-chemical reaction upon a true one in the first sense. Bunsen and Roscoe, in their experiments, used for the calculation of the extinction the exponential formula (p. 144), which is only valid for monochromatic radiation. Burgess and Chapman[2] have repeated the experiment under conditions not involving Bunsen's and Roscoe's assumption, and find "that the light absorbed by mixtures of chlorine, either with hydrogen or with an inert gas such as oxygen, is almost the same as it would be if the diluting gas were absent. There is no indication that the light which brings about the chemical change is distinct from that absorbed by the chlorine in virtue of its optical properties. The energy which brings about the chemical change is derived from the light absorbed by the moist chlorine." If there is any difference in the transparency of a mixture of equal proportions of air and chlorine, and one of hydrogen *plus* chlorine it is of an order which cannot be detected actinometrically. Whilst apparently conclusive in the case of hydrogen *plus* chlorine this result leaves the general question still *sub judice*, for the union of hydrogen and chlorine is not a true reversible, photo-chemical reaction, but a so-called catalytic light-reaction, at any rate in absence of ultra-violet rays.

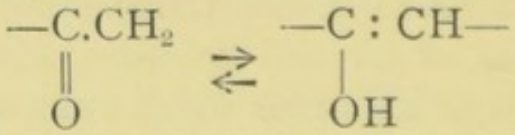
It is evident, however, that light corresponding to the chemical work must vanish, and here we might speak of photo-chemical extinction in Bunsen and Roscoe's sense.

Now, Baly's theory of isorropesis is practically identical with the theory of photo-chemical extinction. Or rather it at once begs and solves the problem, in that it assumes *all* selective absorption to be essentially photo-chemical, *i.e.* it inverts the

[1] Berthelot compares the action to that of a detonator on an explosive mixture.

[2] *Trans. Chem. Soc.*, **90**, 1430 (1906).

Draper law, and might be stated in the form, *all selectively absorbing bodies are light-sensitive* with, however, a somewhat modified meaning attached to chemical change. It is evident that we must examine this proposition more closely. Baly and Stewart [1] point out that, in order to start the isorropesis, there must be some disturbing factor to influence the residual affinities involved, or, as we might put it, there must be an energy gradient. As was stated, Baly attributes *all* cases of colour or selective absorption to the oscillation between the residual affinities on atoms or groups of atoms in juxtaposition. (As we shall see, this is also essentially the explanation which physicists have adopted for the explanation of selective absorption and emission, substituting electrons for residual affinities.) But as Baly and Collie [2] point out, "the reasoning advanced only refers to the conditions when the substance is absorbing light. The vibrations causing absorption must cease when the light is removed or the substance would be self-luminous in the dark." Hence it is suggested that the process of tautomerism is itself dependent on the absorption of light, and ceases when the light is removed. That is, the reaction



is essentially a photo-chemical reaction, and if we like to put it so, light is absorbed in virtue of the reaction, which therefore shows reaction-colour and photo-chemical extinction. But to state, as has been done, that if such photo-chemical extinction exist it would be possible for colourless original substance to give colourless products in light, and only be coloured during and in consequence of the reaction, and hence to contradict the Draper absorption law, appears to be only erecting a false antithesis on a misuse of terms. A body *is* only coloured, *i.e.* selectively absorbing, when light is incident, the phrase has obviously no meaning applied to the same body in the dark, except that it is potentially coloured or capable of absorption by virtue of its chemical constitution.

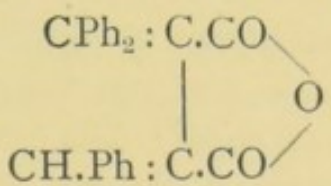
[1] *Trans. Chem. Soc.*, **89**, 513 (1906).

[2] *Ibid.*, **87**, 1332 (1905).

Baly and Stewart further suggest that fluorescence is a manifestation of isorropesis; that is, in selective absorption it provides the mechanism, whilst light actuates it; in fluorescence, isorropesis does both, to a certain extent. We must, however, discuss the relation between isorropesis and emission more fully. Meanwhile we may note, that assuming fluorescence to be due to some such reaction as

$$\underset{\text{absorbing light}}{\text{A}} \rightleftharpoons \underset{\text{emitting light}}{\text{B}}$$

i.e. to an isodynamic change accompanied by emission, then the observation of Nichols and Merritt [1] that when fluoresceïn and other substances are made to fluoresce by ultra-violet light a distinct absorption of light occurs of the same period as the fluorescent light, is of great importance. For it is definite evidence that the free period associated with the return reaction B → A can produce reaction colour or photochemical extinction. And for those to whom the conception of reaction-absorption is difficult, it may be pointed out that, as shown on p. 178, the transition from A to B involves intermediate phases, bodies which may or may not be fixable according to circumstances.[2] Another possible case of photochemical extinction appears to occur in the phenomenon known as *phototropy*. This was the name given by Marckwald [3] to a change in colour which certain organic substances undergo in light, reverting to their original colour in the dark. A number of remarkable changes among the aromatic fulgides have been described by H. Stobbe,[4] of which triphenyl fulgide is a type—



[1] *Phys. Rev.*, **18**, 447 (1904); *vide* also p. 418.

[2] The difficulty or distinction only arises if we endeavour to separate absolutely the concepts matter and energy, substance and accidence.

[3] *Zeit. phys. Chem.*, **30**, 140 (1899).

[4] "Deutsche Bunsen Ges.," *Samml. zu. Wien*, 1908; *Ann. Chem.*, **359**, 1 (1908).

They pass from orange-red or yellow crystals to dark brown in arc or sunlight, the change being completely reversible. The brown and orange modifications are chemically identical and differ only in the solid state. The modifications can exist in a pure state only in light of the wave-length under the influence of which they were formed. Under all other conditions the substance is a mixture or solid solution of one form in the other. The phototropic change is caused by the light-rays which are absorbed by the modification undergoing change. The equilibrium between two modifications in a mixture depends on the wave-lengths of the light to which it is exposed. This phenomenon—displacement of equilibrium according to wave-length—will be discussed later in connection with O. Wiener's theory of Farben-anpassung or colour adjustment. The important point to notice here is that we have in phototropy a case of isodynamic change related to colour in which, apparently owing to viscosity, the return from the equilibrium in light to that in darkness is comparatively slow, whilst, for example, in tautomeric bodies in solution it is practically instantaneous. To sum up, the conclusions which the chemical study of light-absorption lead to are the following :—

(*a*) The selective absorption of light is intrinsically photo-chemical in that the molecule passes from one state to another. On the general energetic view, we may call this, with Ostwald,[1] a transition from a metastable to a labile condition, with a corresponding diminution of the entropy,[2] or increase of chemical potential. A more specialized chemical interpretation is given by Baly's theory of isorropesis, according to which the absorption is due to the oscillation of the residual affinities of juxtaposed atoms or radicles. This change occurring within the molecule, and not destroying its chemical unity, we might term *homo-chemical;* it is essentially reversible.

(*b*) On this dynamical theory of the molecule and of absorption there is no contradiction between Draper's law and photo-chemical extinction. For the absorption at every point

[1] *Lehrb. d. Allgem. Chem.*, II., 1012 (1903).

[2] As corresponding roughly to different aspects, we might term the molecule "strained," "excited," "polarized."

corresponds to that of a substance which in virtue of the momentary condition of its residual affinities (or its chemical condition) is absorbing light, and the distinction between reaction-colour and body-colour vanishes.

(*c*) The molecule may be so strained, or its chemical potential so raised, that it may undergo an idio-chemical change, such as polymerization, which is also reversible. Or it may, in the presence of suitable bodies, enter into irreversible hetero-chemical reactions, for which the light absorption does not import. Only in the reversible reactions is the phenomenon of photo-chemical extinction, in the narrower sense, to be looked for. The others are the catalytic light reactions.

(*d*) On removal of light, the molecule reverts to its original condition, which retrogression may or may not be accompanied by luminescence, depending apparently on resistance and rate of return. The relation between photo-extinction and chemi-luminescence is necessarily very complicated. The extent to which the molecule on absorption of energy manifests its change of state as heat, hetero-chemical change, light, or other forms of energy depends not only on the molecule itself, but on catalyzers, solvents or medium, temperature, etc. Hence the simple relation between absorption and emission is obscured.

It will be obvious that far more questions are posed than answered in the foregoing synopsis. The problems involved are very complicated, and much more experimentation will be necessary before anything like a clear pronouncement on the relation of the absorption of light to chemical change will be possible. But such experimentation will yield little results of general value if conducted without some guiding principle, though this be only provisory, viz. a hypothesis, "a supposition which we hope will be useful" (Stoney). It would seem that the study of photo-chemical extinction, to which is correlated that of emission, must proceed systematically from simpler to more complex cases, somewhat as outlined in the following scheme :—

Reversible Changes in Homochemical Systems.

It is to be remembered that the dualistic scheme of division utilized here is purely provisional. Just as the invention of a more penetrating gun stimulates the invention of a better resisting armour, and again of a gun which can fire projectiles capable of shattering that, so the triumphs of analysis are synechic with the triumphs of a synthesis inverse thereto.

Provisionally, therefore, the study of the absorption and emission of light in the simpler cases concerns :—

Positive elements, such as the metals, of which the spectroscopy is being thoroughly studied at present. The variation in the spectra of sodium vapour, potassium vapour, etc., according to the conditions of excitation, and according to the nature of the light-sources used to excite "fluorescence-spectra" therein, is likely to suggest very interesting possibilities in the way of observing and conducting specific chemical reactions at a distance.

This study is complementary to the spectroscopy of the negative elements, chlorine, bromine, etc., and following this, of the amphibolic or more or less neutral elements, such as carbon, the indifference of which is more or less compatible with the notion that they are constituted somewhat like the "inner salts" familiar in organic chemistry, by a sort of mutual annihilation and fusion of the antagonistic potentialities of positive and negative sub-elements.

The problem of absorption, and its relation to isodynamic change, is being studied for bodies recognizedly subject to tautomeric pulsation, as benzene and its derivatives; in criticizing Baly's theory of isorropesis, Lowry questioned the possibility of even an arrangement or rearrangement of bonds, of linkages, in a single body, independent of the presence of a cataclyst.

To the typical reversible reactions in homochemical systems belong also the polymerization and depolymerization of anthracene, styrol, etc., in which, however, the action of solvents must not be forgotten. Amongst reactions very possibly similarly oriented by light, we have the *cis-trans* interchange

of stero-isomers, and the muta-rotations of sugars, which muta-rotations are no doubt dependent upon the variations in the stress of the ether contingent to them.

Irreversible Changes in Heterochemical Systems.

Between so-called complete reactions, or entirely irreversible ones, which means processes accomplishing themselves too rapidly for an observer to get syntonic with their phases—and reversible ones, there are the pseudo-reversible reactions. Examples of these are to be found largely amongst organic photo-chemical reactions.

Such a reaction as $AgCl \rightleftarrows Ag + Cl$ occurring in light is of the nature of a reversible reaction in a heterochemical system, so long as the presence of dissociated silver and halogen in equilibrium with the salt is recognized. But the greater number of irreversible photolyses, in which the final products differ essentially from the initial material, and which cannot be reversed identically, are probably photolytic changes concomitant to some extent with chemical changes occurring independently of light. Such quasi-irreversible reactions are like strips of a stream rising in a desert and disappearing again further on, apparently disconnected, but really parts of a connected and continuous movement.

§ 72. Physical Theories of Absorption.

There is a very intimate connection between absorption and refractivity, or, more comprehensively, dispersion, which appears both in the chemical and physical study of bodies. It will be well to bear in mind the dynamical meaning of the refractive index. If v_0 be the velocity of light in free space, v in a given medium, λ the wave-length in space, l wave-length in the given medium, then—

$$\frac{v_0}{v} = \frac{\lambda}{l} = n$$

the body's refractive index. By dispersion is meant the

dependence of v or (since v_0 is constant) of n upon λ, *i.e.* $\frac{dn}{d\lambda}$, or for ordinary partial dispersions, $\frac{n_1 - n_2}{\lambda_1 - \lambda_2}$. Chemico-physical investigation has shown that there is a very close parallelism between the atomic structures associated with colour and those producing dispersion, in both cases the presence of juxtaposed unsaturated groups being pre-eminent.[1] Evidently we are dealing with the same function in both, and this is fully recognized in the physical theory of dispersion, which is at the same time the theory of absorption.

Anomalous Dispersion.—In so-called transparent bodies, n increases with the wave-length. But if a body possess a strong absorption band, then on approaching the maximum, this from the red end of the spectrum, *i.e.* with decreasing wave-length, the refractive index *increases* greatly. On approaching the maximum of band from the violet end the refractive index *decreases*. With very strong absorption, the whole red end may be more deviated than the blue. This *anomalous* dispersion was discovered independently by Kundt and Christiansen[2] for substances intermediate between metals and transparent bodies, such as aniline dyes and potassium permanganate, *i.e.* those possessing surface colour. Investigation has shown that the dispersion changes continuously through the absorption strip, and the general relation between the dispersion and absorption will be evident from the following curve for the dispersion and absorption of solid *p*.-nitroso-dimethyl aniline (after Wood).[3]

On the theory that light is an undulatory disturbance in an elastic medium, the velocity $v = \sqrt{\frac{e}{d}}$, where e is the modulus of elasticity, d the density. The simple undulatory theory explains refraction in ponderable media, either by

[1] Cf. Brühl; I. Smedley, *Trans. Chem. Soc.*, **93**, 372 (1908). For the relation between refractivity and structure, see S. Smiles, *Relations, etc.*, in this series.

[2] C. Christiansen, *Pogg. Ann.*, **141**, 479 (1870); A. Kundt, *Pogg. Ann.*, **142**, 163 (1871).

[3] R. W. Wood, *Phil. Mag.*, [6] **6**, 96 (1903).

assuming the ether in the medium is of greater *density* (Fresnel) or of lesser *elasticity* (Neumann). It either case it takes no account of dispersion or the variation of v with λ. The modern theories of dispersion, in which the explanation both of normal and anomalous dispersion is attempted, date from Sellmeier, 1872. Common to all is the conception of the synchronized vibration of some units of the ponderable mass system with the vibrations of the ether, in other words, the principle of resonance. Just as a system of tuning-forks, free to vibrate, would take up or absorb sound-waves of the

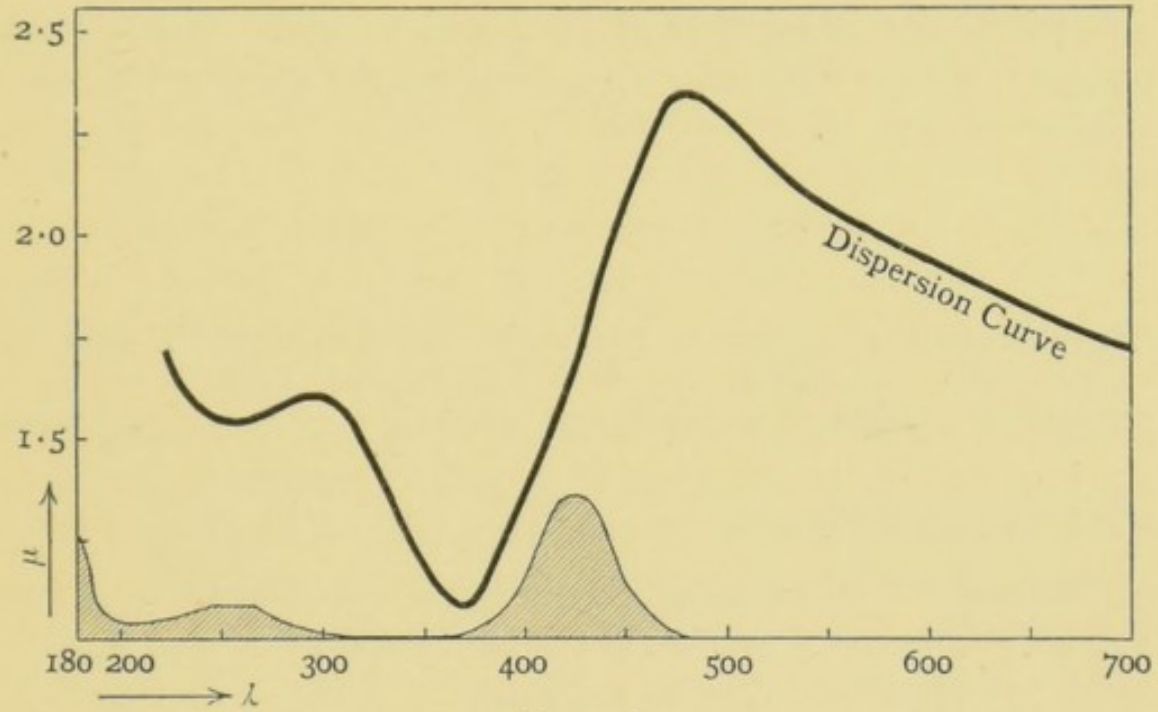


FIG. 26.

same pitch as they can emit, but others only very slightly, so it is supposed that light-waves are absorbed in ponderable media by particles capable of a free period of vibration. Vibrations not synchronized to these only produce forced vibrations of the particles and would hence be but slightly absorbed. For photo-chemistry the interest centres on the regions of strong absorption. The different theories can only be briefly alluded to, but certain conceptions, as of molecular friction, molecular elasticity, etc., which are employed in them continually crop up in the discussion of photo-chemical change, so that some exposition of their physical content seems

desirable. It has been pointed out[1] that all the theories proceed from two fundamental equations, one expressing the vibration in the ether, the other that in the medium. These may be written in the following forms supposing the particles capable of displacements referred to Cartesian co-ordinates :—

For ether, I.

$$m\frac{d^2x}{dt^2} = e\frac{d^2\xi}{dx^2} + \mathrm{F}$$

where m is the mass of the ether particle, ξ its displacement normal to the axis of x, e the coefficient of elasticity, and F a force expressing the interaction of ether and matter. The second equation for the molecular vibrations has the general form—

For matter, II.

$$\mathrm{M}\frac{d^2x}{dt^2} = -hx - \mathrm{F} - \mathrm{F}'$$

The enforced vibration of the molecule, or part of it, may be conceived as that of a pendulum, *i.e.* $\mathrm{M}\frac{d^2x}{dt^2} = -hx$, where h, the proportionality constant, $= \frac{4\pi\mathrm{M}}{\mathrm{T}^2}$, T being its proper period of internal vibration, independent of the reaction of light and matter. The effect of this last is expressed by F, and its sign must be opposite to that of the quantity in the ether equation, from the principle of reaction. Finally, there acts on the molecule a force F′ bringing about the absorption of light. The advantage of this installation of fundamental equations is that we can examine the conceptual content of the different theories by referring to their explanations of the terms F and F′.

The principle of resonance and its consequences were most simply exposed by Sellmeier. The term F′ is introduced to deal with the following difficulty. As the forced vibrations of the particles continue, the amplitude of the disturbance

[1] A. Pflüger, Art. *Dispersion*, in H. Kayser's *Hdbuch. d. Spektroskopie*, vol. iii., 1905.

should increase without limit. Sellmeier supposed that light was not to be regarded as a continuous train of waves, but as formed of irregular series of such trains, separated by pauses—pulses, as they are termed. The amplitude would increase to the end of a train, reaching its maximum in that moment. During the pauses (naturally conceived as extremely short) the vibrations continue, but damped by re-emission. Thus the energy accumulated during the incidence of the wave-trains is lost in the pause by re-emission, and this process, occurring perhaps a million times a second, would cause the absorption. An essentially similar conception—with immensely magnified time units—meets us in the question of the photo-chemical effect of intermittent illumination. To Sellmeier's theory of absorption there are two principal objections, (*a*) the re-emission should always be evident as strong fluorescence, whereas generally it appears as *heat;* (*b*) the absorption should depend on the number of pauses, therefore should vary with the light-source, which is not found.[1]

Helmholz[2] developed Sellmeier's conception by introducing the idea of a bipolar molecule consisting of a heavy central portion, or positive "ion," to which were united one or more negative "ions," which strive to preserve an equilibrium relative both to the central mass and to the ether. Then the terms F and F′ in the fundamental equation are derived as follows: F, expressing the interaction of ether and molecules, equals $\beta^2(x - \xi)$, *i.e.* a constant β^2 multiplied by the relative displacement; further, the absorption resulting in heat is supposed to result from some action similar to friction (quasi-friction) between the mobile and immobile parts of the molecule, and

[1] There is less force in these objections if we make the not improbable supposition, that *when* the *amplitude* of the *enhanced* disturbance reached a certain *critical limit*—a superior limit—that this corresponded to an *absolute change* of character of the form of energy, both (*a*) in wave-form, (*b*) in sensation. That is, such *amplified pulsations* are *identical* with *waves* of *radiant heat*, and yet are identically or consequently equivalent to the installation of "rests" or "pauses," at more or less irregular intervals, in the section of a beam of light. Radiant heat might thus be considered as a summation of infra-red fluorescences.

[2] Cf. Drude's *Optik*., p. 353.

F', the force expressing this, becomes $\gamma^2 \frac{dx}{dt}$, so that the complete equation for the vibrating molecule is—

$$M \frac{d^2x}{dt^2} = - a^2x - \beta^2(x - \xi) - \gamma^2 \frac{dx}{dt}$$

Two important consequences for absorption theory deducible from Helmholz's equation are—

(*a*) The absorption at the maximum will be greater the greater the ratio of F to F', *i.e.* of $\frac{\beta^2}{\gamma^2}$.

(*b*) Large values of the friction-coefficient γ^2 and small values of M (mass of vibrating particle) give broad absorption strips, and conversely.

The qualitative application of these results to the interpretation of absorption spectra is obvious.

Electro-magnetic Theories.—Helmholtz's theory leads over to the electro-magnetic theory and the electron theory of dispersion. On the electro-magnetic theory, the mechanism of absorption is conceived as follows: The absorber is a mixture of ether and molecules, the latter being aggregates of ions carrying invariable electric charges (*i.e.* perfect insulators) which under the influence of the electric force in the light-wave are set into vibration, this vibration being damped by quasi-friction or irradiation (re-emission). Or the molecules, instead of being supposed as composed of perfect insulators, must be conceived as themselves as conductors, with self-inductance and capacity, hence *on their scale*, capable of resonance such as we actually observe with Hertzian waves and bodies of sensible dimensions. Alternating currents set up within the circuit are damped by the Joule heat and re-emission. Here one meets the difficulty of assigning a meaning to the term "Joule heat" in a molecule, involving as it does the statistical conception of temperature, unless the conception of *atomic temperature*, of *inner* temperature, as the vibration-tempo of its electrons, be allowed to apply "below stairs" to the "molecule" and "atom." But, on the kinetic molecule theory, "temperature"

is a measure of the average velocity of translation of the molecules. The former theories may be described as electronic, hence really kinetic-molecular, the latter as molecular-conductivity theories; they are confessedly "conceptual shorthand." Certain important relations of absorption to chemical constitution have been obtained, the relation of which to the theory of *isorropesis* will be apparent. Drude[1] has shown that, extending Helmholz's theory, the molecule may be regarded as consisting of a central positive ion, to which are attached one or more vibrating electrons. The longer vibrations in the infra-red region are assigned to the former, the shorter in the ultra-violet region to the electrons. This hypothesis leads to results for the value of $\frac{e}{m}$, charge per unit mass, in accord with those deduced from cathode ray experiments, etc., and conclusions as to *valency* in agreement with Abegg's modified theory,[2] in that the valency for *cations* is identified with the number of freely oscillating electrons. To account for a discontinuous variation of valency (as with Fe, Mn) it is assumed that the electrons are attached to the central atom with a variable cohesion-intensity. As a corollary from the study of the ultra-red bands, assigned to ponderable masses, conclusions as to the atomic or molecular weight may be drawn. It should be noted that in coloured organic bodies, such as dyes, the visible absorption bands are assigned to the free periods of the valency electrons, or *valons*, as they have been termed by Traube.

The more consequent and recent developments of the electron theory in this connection cannot be dealt with here.[3] The great difficulty remains as to the production of *heat* by the absorption, or the factor F′ in the fundamental equation. Lorentz[4] has attempted to explain this by the idea that the

[1] *Drude's Ann.*, **14**, 677, 936 (1904).

[2] *Zeit. anorg. Chem.*, **39**, 330 (1904).

[3] P. Drude, *Ann. Phys.*, **14**, 697, 936 (1904); *Zeit. wiss. Phot.*, **3**, 1 (1905); H. Erfle, "Optische Eigenschaften u. Elektronentheorie," *Inaug. Dissert.*, Munich, 1907.

[4] See Kayser's *Hdbuch. d. Spektroskopie*, IV., p. 383.

kinetic energy of the electrons is transferred to the molecules, but as the molecules are themselves considered as congeries of electrons, this is only a restatement of the problem or else begs the question. The most promising treatment seems to be that of Planck,[1] who seeks to correlate absorption entirely with irradiation, adopting a statistic treatment of this. As chemists, the essential point made clear is that the absorption of light, or more comprehensively of radiant energy, is essentially and of its nature correlated to chemical affinity and combination, and that in this process, vibration and resonance are the physical concepts involved.

The theories discussed unite in giving, under certain conditions, general equations valid for the relation of dispersion to absorption over a limited range of wave-lengths, and for one absorption-band, *i.e.* the dispersion or refractive index can be calculated from the absorption,[2] or conversely ; the agreement between calculated and measured values, for a region where the optical constants vary enormously over a small range, must not, however, be taken as a proof that the basic assumptions are entirely correct. Data sufficiently accurate for the numerical comparison of different theories are wanting, and the analytical calculation is extremely complicated.

We may regard the molecular-mechanical hypotheses used to found the dispersion theory as stimulative to thought and experiment, but in view of their only partial adequacy for the interpretation of the optical behaviour of stable chemical systems, we must clearly be cautious in applying them to the explanation of *chemical* change in ordinary photo-sensitive reactions. We shall meet the same problems, viewed from the point of view of *emission* of energy, when dealing with the production of light by chemical change.

Kayser[3] has pointed out the difficulty of reconciling the resonance theory of absorption, especially in its molecular-kinetic form, with Kirchhoff's law. For if absorption is

[1] *Ann. d. Phys.*, **6**, 449 (1901).

[2] In the measurement of the absorption it is the extinction-index which is determined (*vide* p. 138).

[3] *Hdbuch.*, **3**, Chap. I.

due to damping, involving change of vibration, it should be the greater the greater the damping. Hence, non-emission of the waves absorbed, whereas Kirchhoff's law asserts just the contrary, Kundt's law or rule for the displacement of the absorption toward the red with increasing refraction of the solvent is a necessary consequence of any of the complete dispersion theories. Thus if the molecule be regarded as a Hertzian resonator, the oscillation frequently will depend upon the refractive index of the medium, *i.e.* its dielectric constant, as has been shown for long waves allowed to impinge upon a grating of metal strips immersed in different liquids.[1]

§ 73. Relation of Optical Activity to Absorption.

It has been found by Stewart[2] that there is a certain connection between the optical activity of organic bodies and their absorption of light, which he expresses as follows :—

(*a*) Within limits, a close relation exists between the absorbing power and the molecular rotation of two substances.

(*b*) The presence of ethenoid —C=C— linkings increases both these qualities.

(*c*) Of stereo-isomers, the one having greater absorption has the greater molecular rotation also.

Now, ordinary non-polarized light is equivalent to a *racemic* mixture of the dextro- and lævo-components, *i.e.* it consists of equal quantities of the opposite circularly polarized Fresnel rays. It was found by Cotton,[3] with copper and chromium potassium tartrate, that there was an unequal absorption of the two components ; thus for ↻ (dextro) polarized Na light the value of $\frac{I}{I_0}$ was 0·0077, for ↺ (lævo) polarized light, 0·0059, and Stewart's results are in agreement

[1] Aschkinass and Schaefer, *Drude's Ann.*, **5**, 489 (1901).

[2] *Trans. Chem. Soc.*, **82**, 208 (1901).

[3] A. Cotton, *C. R.*, **120**, 989, 1044 ; *Ann. Chim. Phys.*, [7] **8**, 347 (1896).

with this. The light transmitted by an optically active solution, owing to the unequal absorption, will be elliptically polarized.[1] Proceeding from the idea that with a racemic compound sensitive to light the effect of *circularly* polarized light would be to remove the corresponding component, thus leaving the mixture optically active, experiments have been made by Byk[2] and others to effect the complete asymmetric synthesis, but so far the results are negative. It is suggested by Byk that the *dextro*-nature of vitally synthesized compounds might be due originally to an excess of lævo-polarized light in skylight.

§ 74. Absorption Spectra and Magnetization.

It has been pointed out that the most markedly selective absorbing inorganic substances—such as the rare earth compounds—which show in the solid and dissolved condition extremely narrow absorption-bands, belong to the paramagnetic series,[3] a connection of as yet unexplained importance. It is not surprising, therefore, that the absorption-spectra of these substances show pronounced and complicated Zeemann effects in a magnetic field of great strength,[4] at the temperature, however, of liquid air. The phenomena are too various to deal with here, but it is important to note that the Zeemann effect is not independent of temperature nor of the anion; the values of $\frac{d\lambda}{\lambda^2}$ vary considerably, but for a field of 40 kilo-gauss are of the order 10 cm.$^{-13}$, and that the corresponding fluorescence

[1] On rotational dispersion in absorbing media, cf. P. Drude, *Optik.*, p. 382.

[2] A. Byk, *Zeit. phys. Chem.*, **49**, 641 (1904); F. Henle and H. Haakh, *Ber.*, **41**, 4261 (1908); P. Freundler, *Ber.*, **42**, 433 (1909).

[3] H. Kayser, *Hdbuch. d. Spektroskopie*, **3**, 1905; H. du Bois, *Rapp. Congr. de Phys.*, **2**, 487 (1900).

[4] J. Becquerel, jn., *C. R.*, **142**, **143**, **147** (1908), and *Phil. Mag.*, [6] **16**, 153 (1908); J. Becquerel and K. Onnes, *Versl. Kon. Akad. Wiet. Arnst.*, **16**, 678 (1908); and H. du Bois and G. J. Glias, *Ann. Phys.*, [4] **27**, 233 (1909).

bands show exactly the same changes, both of $d\lambda$ and of change of polarization, another instance of the intimate relation of absorption to fluorescence.

The relation of optical activity to photo-chemical change in organic bodies—the central of the problems of bio-syntheses—will be briefly discussed later, in view of a certain suggestion as to the relation of carbon to the remaining elements.

§ 75. On Photo-chemical Absorption and Dispersion.

The comparative failure of purely physical considerations to deal with the absorption and dispersion of light may, perhaps, lead to a unitary physico-chemical conception of the process. The physical theories fail to interpret the chemical process by reason of their assumption of a preformed stasis or mechanism in the system corresponding to the stationary or steady state which is observed, whereas actually it appears that the steady condition and the apparent structure is brought into existence by the light acting; in other words, every absorption of light induces a dynamic equilibrium, there being enforced a succession of "false" equilibria, out of which, given sufficient *time*, a "true equilibrium" constructs itself. This "true equilibrium" *is* the chemical *species* adapted to a *definite* field of radiation. Modern organic chemistry points strongly to the deduction that the number of *possible* chemical *species* is *unlimited*, although the actual number isolated is *limited* by conditions of expediency. Recent experiments on the reaction between chromic acid and quinine in light throw some light upon the process.[1] It is found that with a small thickness, such that absorption is not complete, the maximum velocity (current) coincides with the maximum absorption, or minimum of transmission, but that if a sufficient thickness for complete absorption is taken, then the maximum velocity lies away—in this case toward the shorter wave-lengths—from the previously determined maximum of absorption. That indicates—in agreement with Byk and Luther—that the dispersion-curve rather than the absorption-curve corresponds to the chemical

[1] Private communication from Prof. R. Luther.

change. The difference is only in the time of adjustment of a stationary condition. A thin layer, kept at constant volume, will always tend to produce a band of absorption, or a layer with metallic reflection for a part of the incident energy, which will depend upon its own nature and dimensions as well as upon the nature of the incident radiation. It thus tends to approach to the condition which is expressed by Kirchhoff's law, but does not attain it.

[1] Cf. the shift of the visibility function observed on interposing a sodium flame in the path of helium D_3. R. W. Wood, *Phil. Mag.*, Sept., 1904.

CHAPTER VI

STATICS AND KINETICS OF PHOTO-CHEMICAL CHANGE

§ 76. Photo-chemical Change.

It has been pointed out frequently that the distinction between the terms "chemical" and "physical" is arbitrary, being, like all classifications, a mental convenience or economy of thought. Whether we term a particular change brought about by light chemical or physical, will depend upon the way in which we wish to examine or utilize that change. As chemists, we may consider that all absorption of light alters the chemical potential of a system, but whether a chemical change, in the sense of the production of substances with new properties occurs, depends upon a variety of accessory factors. Although pure substances are largely ideal conceptions, it is convenient to consider the action of light, as outlined in the preceding section—

(*a*) On homo-chemical systems (hylotropic phases or like molecules);

(*b*) On hetero-chemical systems, *i.e.* on the molecular theory, different molecular species present.

Experience shows that light can bring about every variety of chemical change; polymerization, or association of like molecules, as in the case of anthracene to dianthracene, oxygen to ozone; but also depolymerization, in that ultra-violet light decomposes ozone; allotropic change of the elements, as with phosphorus and sulphur; isomeric change, as in the transition of maleinoid to fumaroid forms; hydrolysis

(taking up of water), as with salt solutions of the heavy metals, or in the action of acetone on water in light—

$$CH_3.CO.CH_3 + H_2O = CH_3.COOH + CH_4$$
acetic acid methane

It will also give rise to oxidation, as in the case of $PbS + 2O \rightarrow PbSO_4$; reduction, as in the cases of silver, iron salts, etc.; associations and syntheses, as with H_2 and $Cl_2 \rightarrow 2HCl$; dissociations, as $2HI \rightarrow H_2 + I_2$. Hence no classification based upon the conventional types of reactions can be of much use. This multiplicity of effect is a natural consequence of the absorption law, since in mixed or heterogeneous light of all vibration-frequencies the *selective* light-absorption of the chemical system will determine the reaction; whether any relation of the *locus* (in the spectrum) of the absorption to the nature of the change can be deduced will be discussed later. That such a relation is immanent in the phenomena we have every reason to believe, and also that its general form will be consonant with the two laws of thermodynamics; further, from electrical analogy, the law of induced currents is likely to yield a proximate relation. The important relation between photo-chemical change in a sensitive system and the *diffusion* or osmotic-gradient in the same, which will now be discussed, suggests that in plant growth the photo-lytic decomposition may automatically control the diffusion within, that, in point of fact, a plant's *nervous system* is largely in the atmosphere around it.

§ 77. The Measurement of Photo-chemical Change.

As a rough but comprehensive definition of a photo-chemical reaction, we may consider as the change of a system A to B, it being agreed that B is a chemically different individual from A, under the action of radiant energy. Then the reaction will be measured by the proportion of B produced from A, whereby we can use any definite property of B to determine its quantity at any time, or we may observe the diminution in A in a similar manner. Such measurements

are essentially parts of the study of chemical dynamics, and for general details the reader is referred to the volume by Mellor in this series.[1] The quantitative study in this manner of certain reactions has led to the deduction of certain fundamental phenomena evident in photo-chemical change and also to methods of determining the chemical intensity of light. There are, however, certain special factors in the kinetic analysis of photo-chemical change which impart to it a special character and peculiar difficulties to its study. These are, in a word, the effects of the dimensions of the system studied, on the progress of change, effects due to that very absorption of light which brings about the change. For the sake of example we will consider the case of a homogeneous monomolecular change in homogeneous solution affected by light.

Light is supposed to be incident from the side marked with the arrow. Then the change A → B (disregarding any possible reverse action) will proceed at different rates at each thickness *d*, in consequence of the varying absorption of the light (p. 143), so that if we denote the velocity of change by $\frac{dB}{dt} = K[A]$ where K is a function of the light intensity and quality, then K will also be a function of position. And further, owing to the varying velocity in the different layers, concentration differences will be set up, which will tend to equalize themselves by diffusion, so that the light-absorption itself will be constantly changing in a manner dependent on the dimensions of the system. The experimental and analytical methods which may be employed to allow for these factors will be considered in the following. But before passing to this, it may be pointed out that there is a way of looking at the question which puts it on a simpler and more general footing. This is, for the question in hand, to regard light as a *substance*, its absorption as essentially similar to the diffusion

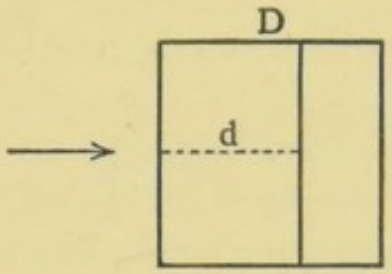


FIG. 27.

[1] *Chemical Statics and Dynamics* (Longmans, 1905).

of a gas (*partly influenced by convection*) into a fluid. Its chemical *intensity* at any point corresponds then to its "active mass." This will be the light *absorbed* per unit of extension. On this view, ordinary absorption is equivalent to the *solution* of the substance "light," just as NH_3 dissolves in water. The further reaction of such a gas as chlorine with water is then the analogy of the photo-chemical reaction.[1]

The general theory of the kinetics of reactions is based upon the "mass law" of Guldberg and Waage, according to which, in homogenous solution, the rate of reaction is proportional to the "active masses" of the reacting molecular species; for these "active masses" we can in general substitute the concentrations (mass per unit volume). Then the most general equation for the velocity v is—

$$v = \frac{dx}{dt} = Kc_1^{n_1}c_2^{n_2} \ldots - K'c_1'^{n'}c'^{n'}$$

$c_1, c_2 \ldots$ being the concentrations, n_1, $n_2 \ldots$ exponents, derived from the stoichiometric equation and expressing the order of the reaction. But before applying this to photo-chemical change we must note—

(*a*) That the reaction may proceed in stages $A \rightarrow B \rightarrow C$, when the separate velocities of the consecutive reactions may be comparable, or one may be so much slower than the others as to determine the rate experimentally measured.

(*b*) There may be side-reactions, with different resultants—

$$A + B = AB$$
$$A + C = AC$$

of which either will be the side-reaction according to which is considered principal.

(*c*) There may be *catalysis*, in fact one may say there always is. This phenomenon is so important photo-chemically that we shall have to study it separately and see what meaning is to be assigned to it from a photo-chemical standpoint.

Hence, apart from the incidence of light, all the varieties of the course of so-called *dark* reactions may be expected.

[1] Such an analogy must not be taken *au pied de lettre*.

Returning to our fundamental equation, the simplest formulation is that the velocity-coefficients K and K′ are, for light of the same quality, proportional to the intensity, but this intensity will be a function of position in the system, as stated, owing to absorption. This formulation, used by Wittwer[1] in his study of the decomposition of chlorine-water by lights, and generalized in the above manner by Nernst,[1] may be termed the Nernst-Wittwer conception. Reverting to the substantial treatment just indicated, it will be seen that the *intensity* of light represents its *active mass* or concentration. As will be shown later, this can be given a molecular interpretation by assuming it to be the concentration of free electrons released by light.

There is, however, another formulation, at first sight irreconcilable with this. Supposing photo-chemical change to be analogous to electrolysis, then the change or decomposition might be simply proportional to the *light absorbed*, *i.e.* the current, and independent of the mass of reacting substance, which is the well-known Faraday law of electrolysis. This conception was advocated by van 't Hoff, and has been developed by Luther and Weigert.

It will be obvious that the kinetics of photo-chemical change are necessarily very complicated. Hence great care must be taken in interpreting the results. It is easy to place too much reliance upon the coincidence of numerical values observed and calculated as confirming the derivation of the particular reaction-equation used. Quite different assumptions as to the nature or mechanism of a reaction will often yield the same analytical formulation. As a particular example, very pertinent to photo-chemical change, we may note that many reactions in gases (thermal dissociations), as, for example—

$$4PH_3 = P_4 + 6H_2,$$

proceed according to the monomolecular function—

$$\frac{dx}{dt} = K(a - x),$$

[1] *Theoret. Chem.*, 4th edit., p. 732.

from which it was assumed that the reaction determining the velocity was—

$$PH_3 = P + 3H,$$

the phosphorus and hydrogen then combining to whole molecules with enormous rapidity. But the great influence which the walls of the containing vessels exert upon the velocity as well as catalyzers upon these walls, make it probable that the actual reaction occurs with great velocity on the surface of the walls, and what is actually measured is the *rate of diffusion* of the gas to the reaction-surface, which would, by Fick's law, be simply proportional to the concentration at any time giving the same equation—

$$\frac{dx}{dt} = K(a - x)$$

as the monomolecular hypothesis. As we shall see, this result is of great importance for many photo-chemical changes.

We may, for purposes of study, roughly divide photo-echmical reactions into—

(*a*) Reversible reactions, *i.e.* formation of an unstable system reverting to the initial state when light is removed. Work is done against affinity.

(*b*) Irreversible reactions, acceleration of change to a more stable state. These must be subdivided into—

(*α*) Complete reactions;

(*β*) Pseudo-reversible reactions.

A completely reversible reaction may be defined as one which occurs only under the influence of light, the system returning to the dark state on removal of light, *i.e.* the dark state must be repeatedly recoverable by intermittent illumination and darkening in a hermetically closed space.

The symbol

$$A \underset{\text{dark}}{\overset{\text{light}}{\rightleftarrows}} D$$

typifies this, of which the polymerization of anthracene to dianthracene is an example. If we regard *light* as a

component, we may note that it is not identically recovered on reversal, so that the reaction is *homodrome* as regards the substance, *heterodrome* as regards light.

As a pseudo-reversible light-reaction, we may take the reduction of ferric oxalate—

$$Fe_2(C_2O_4)_3 \xrightarrow[\text{light}]{} 2FeC_2O_4 + CO_2$$

to ferrous oxalate. In the dark, ferrous oxalate solution is again oxidized by oxygen of the air to ferric oxalate, so we have—

$$A''' \xrightarrow[\text{light}]{} A'' + x$$

$$A''' \xleftarrow[\text{dark}]{} A'' + y$$

and the reaction here is *heterodrome* with regard to the light-sensitive substance also.

A case of a complete reaction is that of $H_2 + Cl_2 = 2HCl$ in light, HCl being stable. For actinometric purposes, the most suitable reactions are such in which the products are directly removed as soon as formed from the reaction-sphere, and the reacting mass is maintained constant. The effect is then simply proportional to the light-intensity. The closest approach to this is obtainedin Bunsen and Roscoe's actinometer, using a mixture of H_2 and Cl_2 brought to a special condition and removing the HCl by water (*vide* p. 268). It has been pointed out by Luther and Plotnikow[1] that very probably the chemical processes in the retina belong to the pseudo-reversible reactions. The function of the eye is essentially that of a self-adjusting actinometer. The necessary removal of the products in an irreversible process by diffusion would entail a large consumption of material. Much more economic are the pseudo-reversible reactions in that the regeneration is effected by a side-reaction, and diffusion has only to supply the agent of this and remove its product. Occurring much more frequently than the true reversible

[1] *Zeit. physik. Chem.*, **61**, 515 (1907).

reactions, there is thus greater probability of the organism using them to form a quickly reacting eye, so advantageous in the struggle for existence.[1]

§ 78. Polymerization of Anthracene.

The peculiar interest of the polymerization of anthracene by light lies in the fact that we have here a reversible reaction in homogeneous solution, in which a definite stationary condition depending upon the light-intensity, is ultimately reached. The reaction, formally expressed, is—

$$2C_{14}H_{10} = C_{28}H_{20}$$ [2]

In darkness, the dianthracene, which is much less soluble than anthracene, reverts spontaneously to the former—

$$2A \rightleftarrows D$$
in light in dark

The reaction proceeds in boiling organic solvents, such as phenetol (b.p. 170° at 745 mm.), anisole (154°), xylol (140°), with a measurable velocity on illumination by the ultra-violet light of an arc lamp, or from a mercury vapour lamp. The anthracene and dianthracene were separately determined, as at low temperatures their rate of change is very slight.

The vessels used were cylindrical in shape and made of thin white glass, 18 cm. long, about 27 mm. outside diameter.

The dark reaction, $D \rightarrow 2A$.

This was found to be monomolecular at all temperatures—

$$K' = \frac{1}{t} \log \frac{c_0}{c}$$

and practically complete; the dependence on temperature given by—

$$\frac{K_t + 10}{K_t} = 2{\cdot}8.$$

The light reaction, $2A \rightleftarrows D$.

[1] If the phototropic process noted later is a pseudo-reversible reaction, it is possible that the visual substance is of this character or a mixture.

[2] For literature, etc., see L. and W., *loc. cit.* The light polymerization was first noticed by J. Fritzche, *Journ. prak. Chem.*, **100**, 337 (1866).

As stated, a "stationary condition" depending upon the light-intensity and other factors is reached. We reproduce one of Luther and Weigert's tables, and will then discuss the factors involved.

TABLE XIII.

Solvent anisole, b.p. 154°. Deff. arc lamp.

1	2	3	4	5	6	7	8	9	10
No.	hrs.	*d* cm.	g.	*h* cm.	C_A	C_D	ΔC_D	*r*	K
35	14	32	25·5	5	58·9	7·9	+ 1·87	1·24	19
41	28	32	25·3	5	31·2	8·79	− 0·98	1·24	21
45	$13\frac{3}{4}$	32	20·7	4·1	52·4	8·95	+ 1·17	1·24	22
46	$13\frac{1}{2}$	16	25·5	2	43·6	11·65	− 1·70	1·24	18
47	$13\frac{1}{2}$	32	25·2	2	40·9	3·19	− 0·05	1·24	19
								Mean	20

In the table, the data are as follows :—

(1) Number of experiment.
(2) Time of illumination.
(3) Distance of wall of vessel from arc in cms.
(4) Weight of solution in grams.
(5) Height of illuminated column in cms.
(6) Equilibrium-concentration of A
(7) " " D } in millimols per litre.
(8) ΔC_D = change in concentration of D from start. }
(9) Radius of cylinder *r* cm.
(10) K a constant.

Discussion of the Equilibrium Conditions.

If the liquid be strongly stirred there will be at equilibrium a mean value of the light-intensity, since each portion will be passing through all values of the light gradient in the solution.

We may, conformably to the general plan of radiant exchange (*vide* p. 77), group the factors into two divisions.

Radiation Factors.—d, distance of lamp, s surface, r radius of cylinder, l = length of illuminated layer, I = intensity of light.

Dimensional Factors of Interior.—G = weight of solution, C_A anthracene concentration, also nature of solvent, temperature, stirring (rotation velocity of unit volume of system).

Consideration of the experimental results shows that if those factors are set constant which remained so in one experiment (light-source, solvent, temperature, and stirring), then the concentration of dianthracene at equilibrium is given by—

$$C_D = K \frac{\text{light-strength} \times \text{surface}}{\text{volume}}$$

Hence $$C_D = K \frac{2rhs}{d^2 g} = K \frac{2}{d^2 r\pi}$$

for diaphragmed undiaphragmed actinometers

whence $$K = \frac{C_D d^2 g}{2rhs} = \frac{C_D d^2 r\pi}{2}$$

when s = specific weight of solvent at boiling-point.

Velocity Considerations.—The influence of temperature on K was considerable.

$$\frac{K_t + 10}{K_t} = 0{\cdot}34$$

For *concentrated* anthracene solution, where there is complete absorption (containing more than 100 millimols per litre), K is independent of C_A.

Velocity of Transformation.—The velocity at the commencement is determined by the same factors as the equilibrium; it can be represented by the empirical equation $\frac{dk}{dt} = K_L - K'x$, where $K'x$ is the *reverse* velocity of D → A (non-sensitive), separately determined, whilst K_L is the same function of the variables as K above. The solvent exercised a *specific* influence upon the velocity and the equilibrium.

§ 79. Reaction Velocities in Photo-chemical Reactions. Application of Mass Law.

In consequence of the light gradient in the system, there is strictly no unitary concentration. The equilibration of concentration may be furthered as much as possible by powerful stirring (Gros) or by using very thin vessels (Bunsen and Roscoe, Wilderman); or the dependence of the intensity on the concentration may be calculated. From this it appears that the order (apparent) of a complete (irreversible) reaction is between n and $n - 1$, when the true order is n.

These considerations lead—as will be seen later—to valid equations for the *velocity in complete reactions with small absorptions*. Here the Nernst-Wittwer application of the mass law is justified. But in a reversible reaction, with strong or complete absorption, since *there is no change in K on increasing the anthracene*, it becomes evident that the true law is that the velocity $\left(\frac{d\mathrm{D}}{dt}\right)$ at any instant is proportional to the chemically absorbed light—

$$\frac{d(\mathrm{D})}{dt} = \mathrm{K}\,\frac{\mathrm{I}}{\mathrm{V}} - \mathrm{K'D}$$

As has been pointed out, this formulation is equivalent to the Faraday law in electrolysis; it is, however, not irreconcilable with the Nernst-Wittwer formulation, since the latter can be deduced as a special case from it. Consider a vertical section of the reaction-space, area q, thickness l, at x cms. from a source of intensity I_0. Suppose only one[1] light-sensitive substance A which reacts with the *insensitives* B, C, etc. Then

[1] In nearly every investigation so far, it has only appeared that *one* component is specifically light-sensitive. The complications involved by assuming more than one independent "sensitive" variable can be diminished by the generally justifiable assumption that two or more light-sensitives act as a single complex. Examples are probably $\mathrm{Fe[Hg''(C_2O_4)_2'']}$, since it is certain that neither Hg'' and $\mathrm{C_2O_4''}$ ions are *specifically* light-sensitive; AgBr (dye), where again all evidence points to the formation of a unitary interdependent complex.

the velocity in the small thickness dx, according to the simple mass formulation, is—

$$(\text{I.})\quad v \,.\, q \,.\, dx = \mathrm{KI(A)}^{\alpha}\mathrm{(B)}^{\beta} - q \,.\, dx - \mathrm{K'(C)}^{\gamma}\mathrm{(D)}^{\delta} q \,.\, dx$$

Then assuming monochromatic light, the light absorbed in dx will be absorbed by A alone originally, and—

$$(\text{II.})\quad d\mathrm{J}_{\mathrm{A}} = - q \,.\, d\mathrm{I} = q \,.\, \mathrm{I}m_{\mathrm{A}}\mathrm{(A)}^{a} dx$$

where m_{A} is the molecular extinction-coefficient, and a represents the influence of concentration. If Beer's law holds, $a = 1$. Combining I. and II.—

$$v \,.\, q \,.\, dx = d\mathrm{J}_{\mathrm{A}} \frac{\mathrm{K}}{m_{\mathrm{A}}} \mathrm{(A)}^{\alpha - a}\mathrm{(B)}^{\beta} - \mathrm{K'(C)}^{\gamma} \ldots q \,.\, dx$$

If $\alpha = a = 1$, then *the chemical change will be proportional to the absorbed light.* Or without assuming $a = 1$ (Beer's law), which, however, in general, holds, there will be such a proportionality between the chemical change and the *absorbed* light as to make the absorption "order" and the reaction "order" identical. We have already seen reasons for identifying these (*vide* p. 189), and the study of the kinetics of photo-chemical change emphasize this identity.

Integrating for the total thickness, (A) rendered constant by stirring—

$$(\text{III.})\quad v = \frac{\mathrm{J}_{\mathrm{A}} \frac{\mathrm{K}}{m_{\mathrm{A}}} \mathrm{(B)}^{\beta}}{\mathrm{V}} - \mathrm{K'(C)}^{\gamma}\mathrm{D}^{\delta}, \text{ etc.}$$

This amounts to stating that the "order" of photo-chemical reactions is always 1. Actually, this holds for practically all photo-chemical reactions investigated; and, indeed, there are few reactions which actually agree with a higher ordering (cf. Mellor).

§ 80. Intermediate Compounds and Catalysis.

In ordinary chemical reversible reactions it is usually accepted that a catalyzer cannot displace the equilibrium.[1]

[1] As to the general discussion of this, see J. W. Mellor, *Chemical Statics and Dynamics*, this series, p. 244.

The action of catalyzers is in many cases best explained by the assumption of intermediate stages. But the photo-chemical reaction is a dynamic condition in which the change is *made* uni-polar, *i.e. forced* in one direction, so that displacement by interaction, not only of the "equilibrium value" of the products, but of the ratio of the exponents expressing the order of the reaction, is not only possible but probable, when catalysis intervenes. It is a matter of convenience very often, as to what and how many intermediate stages are assumed. Luther and Weigert considered two possibilities with the anthracene reaction, in which only one intermediate stage was considered—

$$(\text{I.}) \quad \underset{\text{slow}}{A + J_A \rightarrow A_1} \qquad \underset{\text{fast}}{2A_1 \rightarrow D} \quad \swarrow \; 2A$$

i.e. slow isomerization of anthracene, and rapid polymerization of this photo-anthracene to dianthracene.

The velocities of the separate reactions are—

$$-\frac{d(A)}{dt} = \frac{KJa}{V} - K_1(D)$$

$$+\frac{dD}{dt} = K_2(A_1)K^2 - K_1(D)$$

In the stationary state both velocities are equal to o, and since

$$J_A = \frac{I_{tot.} m_A(A)}{m_A(A) + m_1(A_1)}$$

it can be shown that

$$(A) = \frac{m_{A1}}{m_A} \frac{D^{\frac{3}{2}} \sqrt{\frac{K}{K_2}}}{\frac{I_{tot.} K}{V.K_1} - (D)}$$

which on certain considerations leads to

$$(A) = \frac{MK(D)^{\frac{3}{2}}}{D_{lim.} - (D)}, \quad M = \frac{m_{A1}}{m_A} K = \sqrt{\frac{K_1}{K_2}}$$

The second hypothesis is represented by the scheme

$$2A + J_A \rightleftarrows D_1 \qquad D_1 \rightarrow D \qquad D \rightarrow 2A$$
instantaneous slow slow

i.e. anthracene is at every moment in equilibrium with strongly thermally absorbing photo-dianthracene D_1, which slowly transforms to ordinary dianthracene.

By similar installation of equations this gives for the stationary state—

$$(II.) \quad (A) = \frac{M'K'(D)^2}{(D)_{lim.} - (D)}$$

and both give a very similar result for the dependence of the stationary state on the anthracene concentration.

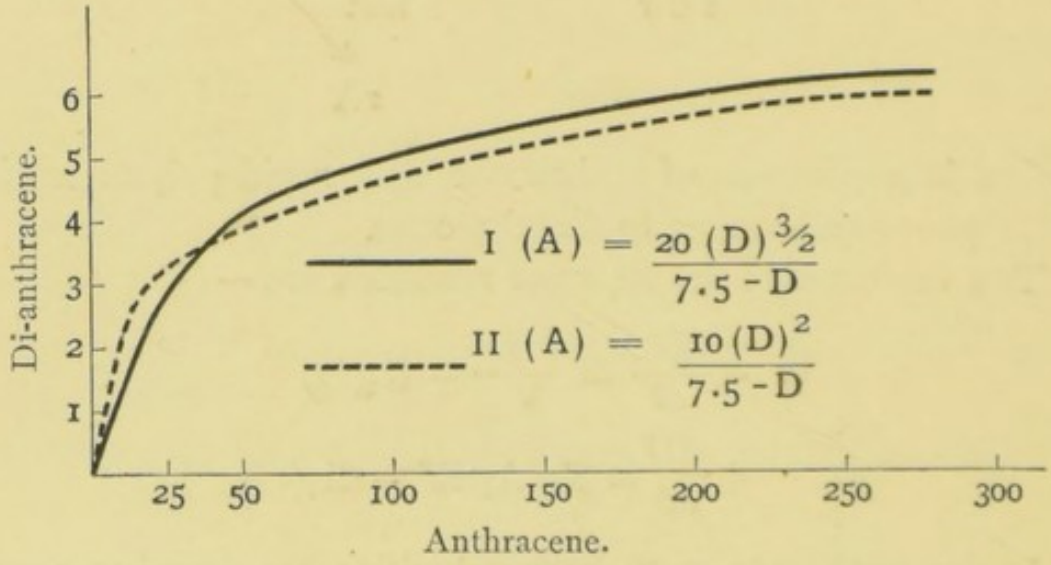


FIG. 28.

The *velocity*, *i.e.* considered integrally, the concentration (D′) of dianthracene at any moment, is given by the same considerations as the concentrations in the stationary state. From equation II.

$$(D') = \frac{K'}{K_2'} \frac{J_A}{V}, \text{ as } K_1' \text{ and } K_3'$$

can be neglected.

Subsequently, however, Byk [1] and Weigert [2] deduced expressions accounting for the phenomena from thermodynamic considerations, without the assumption of the intermediate phase,

[1] *Zeit. phys. Chem.*, **62**, 454 (1908).
[2] *Ibid.*, **63**, 454 (1908).

which, not being isolated, or otherwise demonstrated, was rather of the nature of a mathematical fiction. This assumption, sometimes experimentally justifiable, is a frequent one, both for ordinary and for photo-chemical change, one aspect of it (in relation to constitutional formulæ) has already been noticed, others will be considered when discussing the problem of catalysis in photo-reactions. But further considerations of the phenomenon of phototropy show that a complete study of the equilibrium in light must take into account the reversing action of rays of greater wave-length, *i.e.* that the radiation on both sides must be considered, *since absorption of light by the reaction product can reverse the direction of the change.*

§ 81. Pseudo-reversible Reactions.

The nature of these has already been discussed; we shall now consider the course of one which has been studied with great care by Luther and Plotnikoff, viz. the reaction—

$$(a)\quad HI + \tfrac{1}{2}O = I + \tfrac{1}{2}H_2O$$

followed by

$$(b)\quad \tfrac{1}{2}H_3PO_3 + \tfrac{1}{2}H_2O + I = \tfrac{1}{2}H_3PO_4 + HI$$

Reaction (*a*) proceeds very slowly in the dark, rapidly in light; reaction (*b*) is rapid and uninfluenced by light. It can be shown that the resulting or total irreversible change $H_3PO_3 + \tfrac{1}{2}O_2 = H_3PO_4$ is of practically zero velocity in light or darkness in the absence of the photo-chemical catalyzer HI. The reaction consists practically in the interaction of oxygen (derived from a gas phase) with the reaction mixture of phosphorous acid and hydriodic acid in light. Experiments were made with varying and constant concentrations of oxygen and each individual reaction studied separately. Reactions of this type, where a dissolved gas interacts, offer certain difficulties in the way of ensuring that the gas-concentration in the fluid is a known quantity.

(*a*) For varying concentration of gas (here O_2) the solution is first saturated and the initial concentration determined, then

the concentration at any time is known from the measurements during the reaction (in this case of the iodine).

(*b*) For constant concentration of the gas there must be an arrangement for ensuring a constant saturation by sufficient circulation of the gas phase. Suppose there be a fixed volume of the gas in a burette in sealed connection with the reaction-vessel, then if a constant supply to the reaction-fluid be obtained, the diminution of the gas-volume will be a measure of the gas consumption. This constant saturation was obtained by Luther and Plotnikoff by the arrangement indicated below.[1]

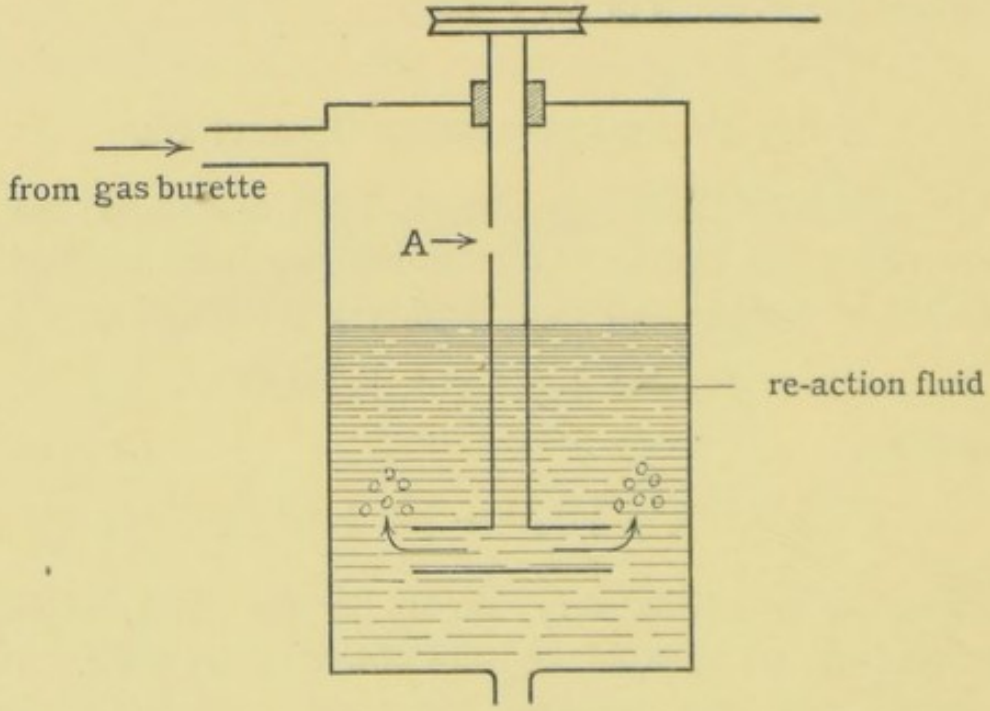


FIG. 29.

The gas is drawn from the fixed volume in the gas burette through the hole A above the fluid level and driven through the liquid in fine bubbles by the rotating centrifugal ⊥ shaped pump. A glass plate inserted (not shown) in the fluid prevents the formation of streaks and whirls. The whole reaction-vessel is sealed off from air and enclosed in a water-jacket through which a constant supply of water from a thermostat is flowing. Two such vessels were then illuminated by the

[1] The apparatus is a very convenient one for many reactions of this type. For full details the paper (*Zeit. phys. Chem.*, **61**, 524 (1907)) should be consulted.

constant upper half of a Uviol mercury lamp.[1] Portions of the fluid could be removed from the second vessel and the iodine determined volumetrically with thiosulphate.[2] The decrease of volume of the oxygen v_t in the burette was reduced according to the usual formula—

$$v_0 = v_t \frac{H - h}{760\,(1 - 0{\cdot}00367t)}$$

(to 0° and 760; h = v.p. of water) and transformed to equivalent weights of oxygen, calculated for $\frac{1}{2}O$ according to the equations. The pump was kept constant at 1500 revolutions per minute.

§ 82. The Individual Reactions.

The separate study of each factor's influence when varied, the others being kept constant, is the only way in which the mechanism of these complicated reactions can be elucidated.[3] The reaction-vessels were compared to ensure that optical equivalence with regard to absorption of light, etc., was secured. The reactions with constant oxygen concentration will be discussed first.

(1) The velocity of the separate reaction between O_2 and H_3PO_3 was found to be practically negligible in the absence of catalysis.

(2) The velocity of the separate reaction between I_2 and H_3PO_3 was measured as follows:—

All oxygen was removed by first insolating the mixtures of H_3PO_3, HCl, and KI. The iodine was powdered in part of the solution, which was then filtered through glass wool into the rest. Only by a preliminary exposure and this filtration could reliable constants in the first stage of the reaction be obtained. It proceeds according to the monomolecular form—

$$-\frac{dI}{dt} = K_2(I)$$

[1] J. Plotnikow, *Zeit. phys. Chem.*, **58**, 214 (1907).

[2] For details and technique of the determinations of reaction-velocities, cf. Ostwald and Luther, *Physico-Chem. Mess.*, 2nd edit., p. 447.

[3] Neglect of this fundamental principle has been responsible for an immense mass of misleading data in photo-chemistry.

in the presence of excess of H_3PO_3, when on integration—

$$K_2 = \frac{\log(I)_1 - \log(I)_2}{0{\cdot}4343(t_2 - t_1)}$$

and is independent of light. The temperature coefficient for ten degrees is 2·94.

(3) The velocity of the separate reaction between HI and O_2 was measured with the concentration of O_2 constant. The mixtures necessarily consumed the same amounts of H_3PO_3 and HCl as in the simultaneous reaction,[1] but the diminution of the oxygen measures the separate reaction alone. *The velocity is directly proportional to the light-intensity*, hence the reaction equation is[2]—

$$\frac{d(I)}{dt} = KI(\tfrac{1}{2}O)$$

As the oxygen-concentration was kept constant and the iodine remained practically so, the change with time is simply linear—

$$KI = \frac{(\tfrac{1}{2}O)_1 - (\tfrac{1}{2}O)_2}{t_2 - t_1}$$

The temperature-coefficient of this photo-chemical change is extremely small.

(4) The simultaneous reaction—

$$O_2 + HI + H_3PO_3$$

The velocity of this will be equal to the sum of the two partial reactions—

$$\frac{d(I)}{dt} = \frac{d(I)_1}{dt} + \frac{d(I)_2}{dt} = K_1I(\tfrac{1}{2}O) - K_2(I)$$

If H_3PO_3 and KI are present in such excess that they may be regarded as constant, then K_1 and K_2 remain constant during an experiment, and the equation can be integrated. The progress of the reaction was followed by titration of iodine from the second vessel.

[1] Cf. also Federlin, *Zeit. physik. Chem.*, **41**, 565 (1902). The dissociation of H_3PO_3 is not sufficientiy known to calculate the concentration of H ions.

[2] In the velocity equations (I) stands for concentration of iodine, I for intensity of light.

Putting $K(\frac{1}{2}O) = K_1$, then the integral form is

$$(I) = \frac{K_1 I}{K_2}\left[1 + \left\{\frac{K_2}{K_1 I}(I)_0 - 1\right\} e^{-K_2 t}\right]$$

where $(I)_0$ is the initial concentration of iodine. If this is nil, the equation has the simple form—

$$(I) = \frac{K_1 I}{K_2}(1 - e^{-k_2 t})$$

The final value of (I) when $t = \infty$ is

$$(I)_\infty = \frac{K_1}{K_2} I$$

Considering only the influence of light, these results may be expressed as follows: "In a photo-chemical pseudo-equilibrium or stationary state, every light-strength corresponds to a definite stationary concentration of iodine, independent of the reaction course. This value is zero in darkness and increases proportionally to the light-strength, becoming zero again in darkness." There is thus a close analogy to the laws of the true reversible photo-chemical processes. The table and curve (Fig. 30) illustrate the course of the reaction.

TABLE XIV.

$(H_3PO_3) = 0{\cdot}530$ $(KI) = 0{\cdot}100$ $(HCl) = 0{\cdot}400$ $H = 753$ $T = 30°$.

Distance of lamp 13 cms.

	$K_1 I$(fd) $= 8{\cdot}9 \times 10^{-6}$.				K_2(fd) 0·0153			
	t_m	(I) $\times 10^3$	(I) calc.	Diff.	t_m	(I)10^3	(I) calc.	Diff.
1	0	0	0	0	0	7·80	7·80	—
	30	0·20	0·18	−0·02	30	4·25	5·12	+0·87
	60	0·37	0·35	−0·02	60	3·13	3·42	+0·29
	90	0·45	0·44	−0·01	90	2·38	2·36	+0·02
	120	0·52	0·49	−0·03	120	1·75	1·68	+0·07
	240	0·60	0·57	−0·03	150	1·38	1·26	−0·12
					180	1·13	1·08	−0·05
	Lamp cut off.				240	0·90	0·78	−0·12
2	300	0·37	Dark		300	0·75	0·66	−0·09
	360	0·20			360	0·68	0·61	−0·07
	480	0·02			480	0·60	0·59	−0·01
	Lamp reinserted.				∝	0·60	0·58	−0·02
3	540	0·36	Light					
	600	0·54						
	720	0·60						

It will be seen that the same equilibrium value of (I) was reached from both sides. Further experiments showed that it was directly proportional to the light-strength, and displaced in favour of the photo-chemical reaction by lowering the temperature.

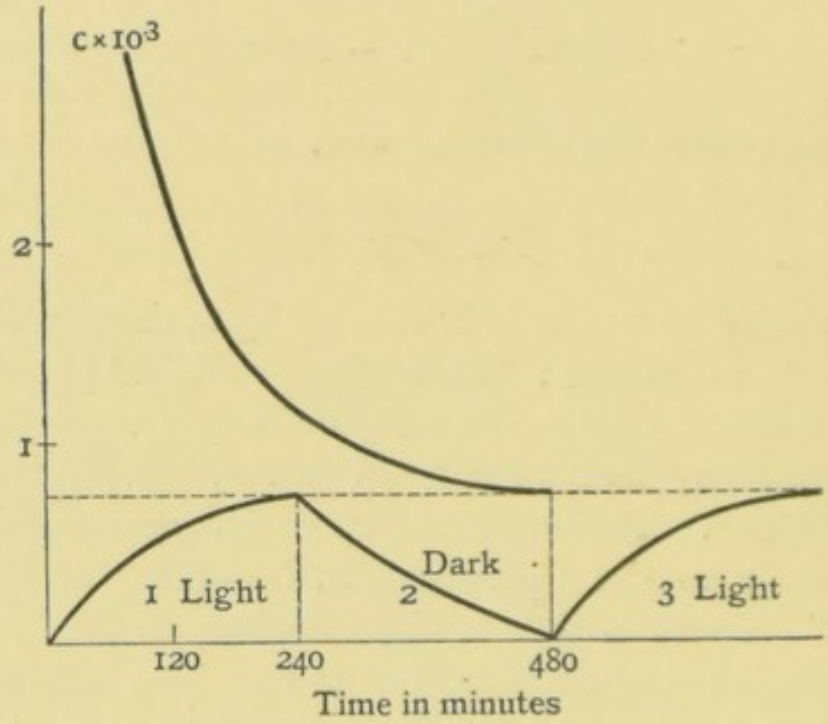


FIG. 30.

§ 83. REACTION WITH VARYING OXYGEN-CONCENTRATION.

When the reaction mixture is originally saturated with oxygen and no further supply is made, the integral assumes a different form, being now—

$$(\mathrm{I}) = \frac{(\tfrac{1}{2}\mathrm{O})_0 \mathrm{KI}}{\mathrm{K}I - \mathrm{K}_2} \cdot (e^{-\mathrm{K}_2 t} - e^{-\mathrm{K}t})$$

where $(\tfrac{1}{2}\mathrm{O})_0$ is the initial concentration of oxygen, $I =$ light-strength, and K and K_2 have the same meanings as before. The curves show a maximum for the iodine concentration (I) (see Fig. 30). The calculated and observed results agreed very well. Another example of a pseudo-reversible reaction is the decomposition of ferric oxalate, which reduces to the irreversible reaction—

$$\mathrm{H_2C_2O_4} + \tfrac{1}{2}\mathrm{O} = 2\mathrm{CO_2} + \mathrm{H_2O}$$

catalyzed by light and iron salts, either of which alone catalyzes but little or not at all. Here iron is the "photo-chemical catalyzer." The kinetics of the reaction—

$$Fe_2'''(C_2O_4)_3 = 2FeC_2O_4 + 2CO_2$$

will be considered later, and its application to actinometry. It is obvious from this that *oxygen* should *retard* the photo-chemical reduction of the metal salts, and this is experimentally borne out. Thus the sensitiveness of Eder's mercuric oxalate actinometer may be increased eighty times in absence of oxygen.[1]

Whilst the kinesis of this reaction is satisfactorily described by the equations of Luther and Plotnikoff, there are probably two sub-reactions not here indicated, but which are essential to it, viz. photo- or optical sensitizing of the reaction by *iodine*, and the induction, which, as was stated, was compensated for by preliminary exposure of the catalyst. It is evident that oxygen plays the same part here as in the reactions between

$$Cl_2 + H_2, \text{ etc.}$$
$$Fe''' + C_2O_4''$$
$$Hg.Cl_2 + Fe''' + n(C_2O_4''). \quad \text{Eder's solution.}$$

It may be said that all autoxidations are so far photo-sensitive, that they may be made sensitive to ordinary light by a suitable photo-sensitizer, *i.e.* a substance having an absorption band in the visible spectrum.

§ 84. Irreversible Processes.

It is to be suspected that in principle all single and definite physico-chemical reactions are *per se* reversible, but in practice, where the essence of the matter is in making one aspect of a possible change real or realizable, the virtual and reversible nature of the independent reaction-elements is masked by their unification in or subordination contingent to the transaction and passage of an irreversible process. It is possible, even if hardly conceivable, that either on the astronomical

[1] Cf. Chr. Winther, *Zeit. wiss. Phot.*, **1**, 709 (1909).

scale of magnitudes extensive and intensive, or in the unpenetrated amicroscopic fastnesses of the atom, there may be an indefinitely near approximation in the working of the *mechané* of nature to the ideal of the perfect thermodynamic cycle,[1] but in actuality there seems a powerful tendency in the workings of those parts of nature that our faculties can subtend to indefinitely postpone and sheer off the singularly uninteresting state of perfection. But in so far as concerns photo-chemical changes, it is as well to indicate that any division of these into "reversible" and "irreversible" changes is primarily provisional and temporary, and that further and intensified investigation of a given reaction may lead to its transposition from the rubric of irreversible to that of reversible reactions. It has become the cardinal principle in regard to physico-chemical changes in systems, in respect of displacements of equilibrium, that the most probable and persistent tendency or drift contingent to all changes or series of reactions is in the direction of forming that system, that state of equilibrium, which has the greatest entropy. Without entering into the mathematical and energetic consideration of the principle of increase of entropy, we may point out a common feature in the aggregate of photo-chemical changes which may be regarded as a corollary to this thesis. That is the tendency which all such changes in quasi-homogeneous systems exhibit to produce products accumulating rather by side-reactions apparently impertinent to the change of principal interest, products heterogeneous in section, and singularly indifferent to light, singularly resistent to solvents and physico-chemical reagents. They are as a class perhaps most comprehensively designated as "fatigue products," and for all that they appear often rather as somewhat objectionable interregna inhibiting the uniform progress of a reaction, their recurrence, in view of their tendency to progressive accumulation with time, their inhibitive influence on the primary reaction, and their unification in species of *membranes*, is perhaps of considerable significance in regard to the main problem of photo-synthesis in nature. In the

[1] See F. G. Donnan, *Thermodynamics*, this series; P. Duhem, *La Mecanique Chimique*, T. 1 (Paris, Hermann, 1898).

process of vegetative metabolism, the common feature is a deposition of tissue encasing matured reserve food-stuffs and canalizing such tissue in the making, the growth being the more prolonged and persistent in the measure of the enforcement of a certain *rhythmic relaxation* of the quasi-explosive, positive or catabolic processes, which, constituting in *effect*, in the propagation of the plant-organism, as a unit of struggle for dominance, its movements always on the whole in the direction of capturing more energy, more power of intensely exerting its function *sui generis*, are, in the matter of *cause*, actuated by autoxidations and decompositions of its proper protoplasm, a physico-chemical aggregate of physiologically *specific*, though physico-chemically somewhat indeterminate composition, a protoplasm which, as Claude Bernard said, must die to live, must die above all that the organism may progress.

The plant world is fundamentally differentiated by the ways in which it accomplishes this encasement in insoluble, indifferent cell-walls—the "fatigue-products" of the strife of its own ascending and expanding effort with the energies of its environment—in a subordinate measure of readily soluble immediate food-stuffs, but, fundamentally, of the mature insoluble nuclei of its specific protoplasm. At the foot of the scale of vegetative life, we have the fission-fungi for which the functions and mechanisms of spread of the species and growth of the unit are identical in the sense of being alternating phases in the same current.[1] The pressure of the catabolic disintegration (in which consists the expansive force and moving energy par excellence of the organism) is here subject only to the simplest type of recurrent relaxation. Wherein consists primarily, in this very relaxation of the catabolic aspect of the change, the genesis of the alternative anabolic process, the encasement of unused energids (energy-masses) in a semi-resting state, as dynamids, if one desire a term to express limited quanta of potential energy, static as compared with the kinetic condition denoted by the term energid. At the head

[1] Consider the dynamical similarity between the morphological unit (or colonial aggregate) of that common fungus, a *puff-ball*, and its physiological unit or cell.

of the scale, we find this simple theme, that of encasement of the energy-centres of the organism, the anabolic process instanter concomitant and continuous by the reversal of the catabolic process, elaborated into the surpassing plenitude and complexity of growth of tropic and sub-tropic forests, and in which the differentiation of function has been carried stages far beyond the humble suggestion of a heterogenesis which is traceable in the asymmetry of direction, rather than direct cleavage of kind, of the vitality of bacteria and fission-fungi, with which it seems chiefly a question of the state of their ambient medium whether intervesicular spread and increase by continued fission take place, or intra-vesicular, intracellular subdivision, culminating again, this anabolic process, in the alternative catabolic process of sporulation.

We have made this interpolation here, to suggest the importance of the formation of photo-anhydrides in regard to the extension of the permanent and persisting tissue-elements, the parenchymatous and allied histological formations, in plant-growth. In the ensuing sections we shall see that the photo-chemical reactions which we are at present considering, initiated and to some extent maintained by coherent radiation from definite light-sources, are continued, subsequent to the cessation or shutting off of such intensive radiation, by complementary processes of chemi-luminescence, and that wherever persistent chemical changes go on, there is considerable reason to credit the continuance of the propagation of radiant energy, of light, invisible and visible, which, in the words of a pregnant saying, "leitet das organische Wesen an." The luminescence concomitant with the decay of organic bodies has long been observed, it is only more recently, in the recognition that the putrefactive process is concomitant with the vital processes of specific bacteria, that we have, in the increasing numbers of photogenic bacteria, acquired the evidence that it is as much a sign of life, of their growth, as a sign of death.

Hence it should be clearly understood that all the automaticity and reversibility specially characteristic of conjugate and reciprocal point-pairs in optical systems is

subjunctive to a velocity of automaticity and reversibility, that is, to the arbitrary selective power and irreversibility of the conditions of vision with human eyes. The distinction between irreversible and reversible processes is a very valuable one, but, like the correlative distinction between involuntary and voluntary processes in a living organism, does not disagree with a constant underlying possibility of a process passing from one class to the other, concomitantly with the march of experience. The self-same kind of distinction crops up in the relation of "true" to "false" equilibria.[1]

Irreversible Processes.

A typical example of an irreversible reaction has already been noticed as contingent to the pseudo-reversible reaction studied by Plotnikoff,[2] namely, the reaction $2HI + \frac{1}{2}O_2 = I_2 + H_2O$. In the presence of great excess of KI and HCl the reaction is of the first order as regards oxygen. Its temperature-coefficient for 10° was found to be 2·86. The empirical velocity-equation

$$-\frac{d(O_2)}{dt} = Kd(O_2)(KI)^{\frac{3}{2}}(HCl)^{\frac{1}{2}}$$

agrees for the kinetics in the dark, where it is also found that HNO_2 has great catalytic influence. In light the reaction remains of the same order as regards the variable substances, with no perceptible induction or deduction; the most active rays are in the blue at 436λ, both the ultra-violet and the rest of the visible spectrum being comparatively ineffective beside these, to the intensity of which the velocity of the reaction is directly proportional. It has, in light, a small temperature-coefficient, 1·4, and is very susceptible to certain catalysts, extremely minute quantities of uranine and eosine, also of copper salts greatly retarding it, whilst quinine, æsculine, and

[1] Cf. J. W. Mellor, *Chemical Statics and Dynamics*, this series, p. 419.

[2] See p. 221.

chloroform are said to accelerate it. The character of the reaction may be summed up by the equation—

$$-\frac{d(O_2)}{dt} = K_1 10^{-0{\cdot}0147T} . J . (O_2)^{\frac{3}{2}}(KI)(HCl)^{\frac{1}{2}}$$

for rays at 436γ.

The influence of catalysts on such a reaction, which as is stated may be either positive or negative, is possibly due to some extent to their proper reactions in light being concomitant with a reaction luminescence either favourable to the forward reaction, or favourable to the inverse one. As already stated, reversibility and irreversibility are provisional and relative distinctions. The study of photo-chemical reactions is, on the one hand, a study of the chemical processes correlative to the gross physical fact of the absorption of light by media—which transition of light from a patent and actual state to a latent and potential state is correlative to an intimate redistribution of the chemical potentials of the absorbing substance; and, on the other, to the chemical processes correlative in the emission of light by media, which gross physical fact is correlative to the inverse process of the release of light from a latent and potential state to an actual and patent one, and, correspondingly, to an inversion of that distribution of chemical potentials of the media such as the fact of absorption betokens. Hence, on the whole, and casting up accounts grossly, we have probably little reason to doubt that the emission and absorption of light complies with the principle of action and reaction. In using the term "chemical potential," we are referring to what is sometimes called the "intensity-factor" of chemical activity and reactivity, but which, as the subtle elusive and ambiguous quality of the linkage between the hypothetical elemental substances out of which ordinary bodies are represented as being made, is often termed "affinity."

§ 85. Actino-chemistry of the Elements.

To the reversible photo-chemical changes belong in general the allotropic changes of the elements induced by radiation, and the various "activifications" and "passivifications" thereof. The discussion of this for gases such as chlorine, oxygen, etc., will be given later. In the solid and fluid states the phenomena are more easily studied, as we say, the changes are *slower*.

Sulphur.[1]—Monoclinic sulphur (m.p. 120°) dissolves in CS_2, is transformed by violet light into the amorphous insoluble form, with evolution of heat (2300 cals.). This reverts in the dark, especially on heating. The equilibrium conditions have been investigated by Rankin,[2] Kruyt, Wigand, and others.[3] The reaction may be expressed by—

$$S_{\text{rhombic}} + \underset{\text{(violet)}}{\text{light}} \rightleftarrows S_{\text{am.}} + \underset{\text{(infra-red)}}{\text{heat}}$$

Beside heat, Rankin found that ammonia and ammonium sulphide catalyzed the reverse action. At 22·5° an equilibrium value for the light-intensity for the change of state of sulphur in carbon disulphide was 5 c.p., at 40° 45 c.p., from which the strong influence of heat on the reverse reaction can be gauged. As is pointed out by Rankin, the phenomena are in agreement with the Phase Rule if light-intensity is taken as a new independent variable. Systems of sulphur in benzole, toluol, etc., show mixing luminescence (cf. p. 384). Sulphur heated above the melting-point shows interesting thermotropic changes of colour, perfectly analogous to the phenomena of phototropy.[4] Wigand, using a hand-regulated alternating arc 35 volts (20–25 amps.), found an increase of

[1] Cf. Schenk, *Zeit. phys. Chem.*, **60**, 631 (1904).

[2] *Journ. phys. Chem.*, **11**, 1 (1907).

[3] *Zeit. phys. Chem.*, **64**, 455 (1909).

[4] A. Lallemand, *C. R.*, **70**, 182 (1870); M. Berthollet, *C. R.*, **70**, 941 (1870); G. A. Rankin, *Journ. phys. Chem.*, **11**, 1 (1907); A. Wigand, *Zeit. phys. Chem.*, **63**, 273 (1908), **65**, 455 (1909) (literature in full); H. R. Kruyt, *Zeit. phys. Chem.*, **64**, 513 (1908), **65**, 486 (1909).

10 per cent. at 118° for $K = \frac{(S_{am})}{(S_{sol})}$ the colour of the fluid modification deepening from yellow to red. As already stated, no change in the molecular weight S_8 could be observed, and the only interpretation consistent with the atomic hypothesis is that of isodynamic isomerism. The photo-chemical changes of phosphorus, selenium, and tellurium are of the same type, but seem to be more complicated.

Selenium.—When precipitated from selenic acid it is a red amorphous powder, easily soluble in CS_2, giving red crystals which do not conduct electricity (m.p. 125°–130°). It passes in light to *selenium-β*, crystalline, with evolution of heat (1400–5300 cals., uncertain). The crystals β melt at 277°, and on heating go back to the α-form. R. Marc showed that the transition temperature $\beta \rightarrow \alpha$ is *ca.* 210°. So far we have the scheme—

$$\text{Amorph. } \alpha + \text{light} \underset{\text{(violet)}}{\rightleftarrows} \text{cryst. } \beta + \text{heat}$$

But if kept at the transition-temperature, a black intermediate complex form is obtained, which conducts well, the conductivity being greatly lessened by light. Hittorf (1852) observed the influence of sunlight upon the transition, and Smith (1873) showed that light increased the conductivity of the red forms, and decreased that of the black form. Siemens prepared very sensitive cells, and the change has been utilized for a method of light telegraphy and telephony, and more recently, with success, by Korn for the transmission of photographs by wire.[1] It is evident that a series of phototropic phases are involved, since very diverse dicta as to the relation of sensitiveness to the *colour* of the light have been given. Each form is stable under light of the colour it is formed by and no other, all being in solution or in a hylotropic phase at the transition point. Shelford Bidwell[2] put forward the theory that the change of conductivity was due to the formation of electrolytically conducting selenides by photo-chemical action,

[1] *Phys. Zeit.*, 1908, p. 789.

[2] Eder's *Jahrbuch d. Phot.*, 1898, p. 374.

but G. Berndt[1] has shown that the most refined purification leaves the sensitiveness undiminished, so that it is the property of the selenium, *per se*. *Tellurium* shows similar changes, but has been but little studied.

Attempts to represent the relation of the conductivity of selenium to the intensity of illumination have not produced a completely satisfactory formula. Hopius proposed

$$m = a\sqrt[3]{I}$$

where m = conductivity, a a constant, and I the intensity of light; and Heschias[2] the formula

$$I = a(b^m - 1)$$

where m = conductivity,

hence $$\log I = \log a + m \log b - c$$

or $$m = \frac{\log I - a - c}{n}$$

§ 86. Allotropic Changes in Light.

Phosphorus.—The yellow A-form of phosphorus melts at 44·4° and is soluble in CS_2. In light it is transformed into the red B-modification (m.p. unknown, insoluble in CS_2) with the evolution of 4400 cals.[3] The transformation takes place independently of the medium, so far as has been ascertained, in complete vacuum, in absence of moisture and at − 14°. The red phosphorus has a higher conductivity. According to Draper[4] and Lallemand[5] the blue, violet, and ultra-violet rays

[1] *Physik. Zeit.*, 1904, p. 121.

[2] *Phys. Zeit.*, 7 (1906), 163, but G. Athanadiadis (*Chem. Phys.*, [4] **25**, 92 (1908)) finds both unsatisfactory over a large range. This is only what we should expect, since a stationary state for the reversing and inciting rays would be formed, but this would be a fluctuating function of the electric convection itself.

[3] Giran, *Zeit. physik. Chem.*, **50**, 489 (1904); *C. R.*, **136**, 677 (1903).

[4] *Memoirs, Scientific*, p. 339.

[5] *Fortschritt. d. Phys.*, p. 400 (1870).

are chiefly active, but the change is also brought about by heat. Whether there is any polymeric change appears uncertain.[1]

B, passive, metallic, good conductor, insoluble. + radiation.	→ ←	A, active, soluble, bad conductor. + light.

Arsenic.—The yellow, soluble form of arsenic is converted by light into a grey or black form, with evolution of 4900 cals. This action is also brought about by heat, so that it appears that the visible, the violet, the ultra-violet and the ultra-red rays are efficient.

B, passive, metallic, insoluble, good conductor. + radiant energy of great frequency (chemism, electricity).[2]	→ ←	A, active, soluble, bad conductor. + radiant energy of lesser frequency (light, radiant heat).

If the elements recognized as undergoing phototropic change are grouped together, certain interesting regularities become manifest. To begin with, the *order* of the phenomenon is a function of the atomic weight for the same group of elements in the periodic classification. Thus in Group VI. according to Mendeléeff[3]—

[1] Cf. Dammer's *Hdbuch. anorg. Chem.*, **4**, 316 (1902).

[2] These equations must not be taken as embodying more than the crudest aperçu of the phenomena of elemental metamorphosis. Not only the vibration-frequency, but the steric disposition, or polarization, of the energy-flux requires consideration.

[3] Cf. J. W. Mellor, *Chem. Statics and Dynamics*, p. 348.

Element.	Atomic weight.	Phototropy.
Uranium . . .	239	Unstudied, but its salts are extremely sensitive to light, and it is the base of radioactive change.
Tungsten . . .	184	Unstudied, but salts photosensitive. Shows passivity.
Chromium . .	52·1	Light-sensitiveness unstudied, but remarkable range of passivity under thermic and electric stimulation. Salts and compounds photo-sensitive.
Molybdenum .	96·0	Exhibits passivity. Salts, etc., light-sensitive.

Turning to the metalloids of this group, the progression in the effect becomes more striking.

Element.	Atomic weight.	Phototropy.
Tellurium . .	127	Very wide range of forms, light-sensitive all through up to long heat-rays.
Selenium . . .	79	Phototropic over range from ultra-violet to short heat-rays. Very sensitive to light.
Sulphur . . .	32	Phototropy more limited, transitions sharper, but strongly marked for radiant heat.
Oxygen . . .	16	Phototropy only shown for very short wave-lengths, but there well marked.

It will be seen that what may be termed the elasticity of the phototropic effect is on the whole less, the higher the atomic weight; as the atomic weight increases, and therewith usually the metallic character, the superficial resistance to phototropic change increases, a metallic glance enabling the substance to simply reflect the incident energy with minimal absorption.

Somewhat similar relations obtain in Group V.

Element.	Atomic weight.	Phototropy.
Bismuth . . .	208	Unstudied, but shows a passive form. Salts slightly sensitive in white light.
Antimony . .	120	Change from active to passive form occurs with explosive rapidity by shock or heat.
Arsenic . . .	75	Change from active to passive form provoked by a wide range of radiation, but slowly enough to be studied.
Phosphorus . .	31	Change from active to passive state easily studied (*vide* p. 235).

The transitional elements of Group VIII.

Fe 56	Co 59	Ni 59	(Cu) 63	All show active-passive oscillations, and form *colloid* solutions of increasing stability as the *atomic weight* increases.
Ru 102	Ph 103	Pd 106·5	(Ag) 108	
Os 191	Ir 193	Pt 195	(Au) 197	

Photo-chemical Allotropy.—As a general rule it may be said that every sensitive substance not already adapted to a radiation-field, tends to form a *reversing layer*, which, by a simple inversion of phase of the incident vibrations, critically reflects them without allowing complete penetration and consequent volume disturbance. This capacity varies from one element to another, and is also a function of the radiation-field itself. Thus, in the cases of phosphorus, selenium, and arsenic, the self-reversal of the element extends throughout its substance, it calmly resigns itself to fate, and passes from an insulating to a conducting state, electrically speaking.

On the other hand, metals, in which the electric conductance and magnetic inductance are usually already high, avoid increase of internal work by superficial oxidation when possible. This process is undoubtedly intimately associated both with the phase-change which light undergoes on reflection from

metallic surfaces, and also with the "passivification" of metals. That is to say, the transition of the elements from an active (soluble, etc.) form to an inactive (insoluble, etc.) form is seldom, if ever, spontaneous, but depends not only on the radiation-field *tending to adapt it*, but involves a *trace* of another substance, which acts as *advocatus diaboli* and initiates the transformation.

§ 87. The Illumination of Photo-chemical Systems.

This will necessarily depend upon the source used and the reacting system. The least efficient method, but most generally employed, is a small source and a diverging beam, the

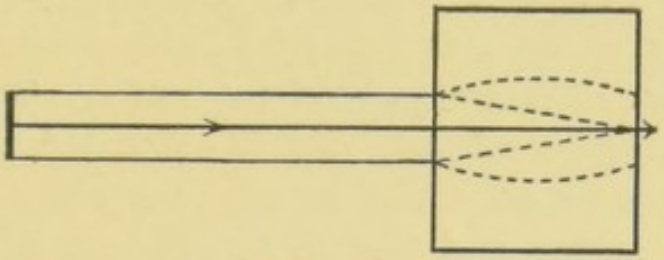


Fig. 31.

calculations being made from the inverse square law. Much superior is the use of a parallel beam of uniform intensity through its section, and of small area compared to the system. It can be made con-axial by a proper lens system, and the energy incident is then simply $\frac{E_0 \times a}{r \cdot R}$, where E_0 is the specific emissivity of the source, a the area or cross-section of beam, r the distance, and R the amount lost by transmission. The small beam has the advantage that there is little or no side loss, and its volume is easily computed. On the other hand, the distribution of intensity is complex in the system itself. To secure a uniform distribution in a plan-parallel walled actinometer, it is best to use bilateral illumination, when, if this is uniform, the two gradients are in the opposite sense, and compensate. Instead of this, the method adopted by nature may be employed, viz. a converging lens to admit light into the system. The absorption by the system then acts in the opposite sense to

the concentration of light by the lens, and a uniform concentration may be secured.[1] The method further permits, for dilute systems, of an examination of the transmitted beam. For distributive powers of lens-systems, see P. Drude, *Lehrb. d. Optik.*, 1900, p. 86; Czapski, in Winkelmann's *Hdbuch. d. Physik. Optik.*, p. 721; Heath, *Geometrical Optics.*

§ 88. Insolation Vessels.

For gases, these may be either cylindrical tubes, for which a con-axial water-jacket[2] may serve as a lens-system, or thin parallel walled vessels, such as were used by Bunsen and Roscoe.[3] For fluids, various forms of parallel walled cells have been used. Where it is desired to operate with gas-free solutions, the difficulties increase. Goldberg has used vessels of plate glass, about 6–8 mm. thick, with a circular aperture of 60–70 mm. diameter pierced in centre. On one side a thin (0·8 mm.) piece of plate glass is cemented, through which the light was admitted, whilst at the back was a thicker piece, backed as a mirror, and with an aperture for filling. Several such vessels could be exposed together on a rotating turn-table, stirring being effected by a short glass rod enclosed (Fig. 32).

With a reflecting back, partial homogenization is secured, the actual planes of change being at the antinodes of the stationary waves engendered by the conflux of incident with reflected wave-trains.

B. Szilard[4] has devised a convenient form for reactions in either homogeneous or heterogeneous systems, and which allows of the introduction or removal of gas or fluid during the reaction. It consists essentially of a one-piece Büchner funnel of glass, the cone having an angle of 45°, with reflecting sides. The surface of the liquid must be a few mm. from the sealed-on top, to prevent adherence of any precipitate which

[1] Not only in the eye but in chlorophyll cells—the chloroplasts—does nature furnish a lens before the actinotropic substance.

[2] For investigations with ultra-violet, quartz must be used. As a thermostat fluid glycerin or metastyrol is fairly diactinic.

[3] *Phot. Untersuch.* Ostwald's *Klassiker*, No. 34, p. 36.

[4] *Zeit. wiss. Phot.*, **5**, 203 (1907).

forms. Gas can be introduced by one tube, and fluid drawn away by another (see Fig. 33).

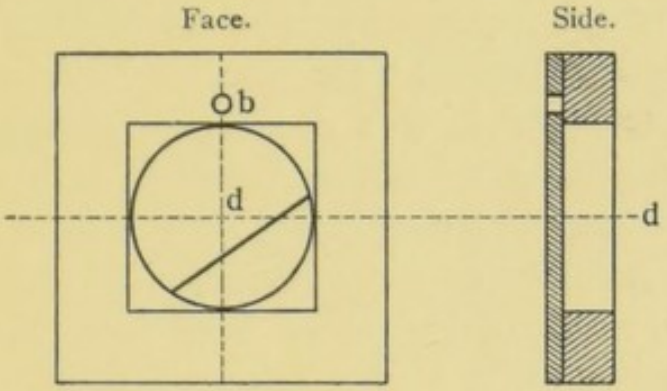


FIG. 32.

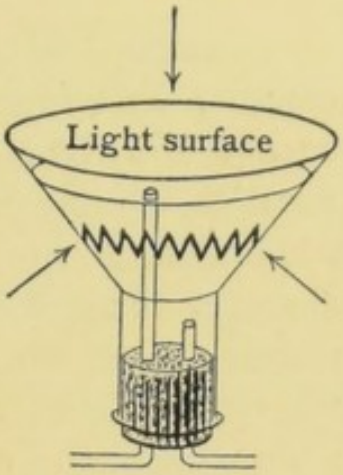


FIG. 33.

The type of actinometric vessel used by Burgess and Chapman [1] in their researches on the combination of hydrogen and chloride, and which resembles in principle that used by Bunsen and Roscoe, is shown in Fig. 34.

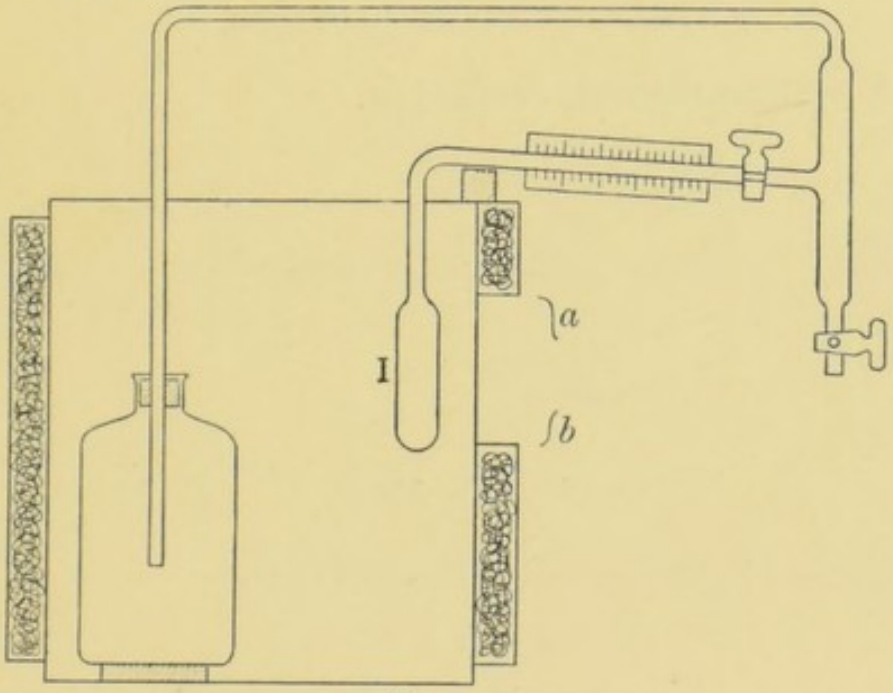


FIG. 34.

The vessel I is the actual insolation-vessel, it is contained in the felt-covered thermostat, exposure being made through the window *a–b*; the manometer-tube also shown is connected up with a large vessel also immersed in the thermostat, so that indications were independent of thermal variations.

[1] *Trans. Chem. Soc.*, **89**, 1426 (1906).

§ 89. Compensation for Absorption.

A method for obtaining the "order" of a photo-chemical reaction by elimination of the asymmetry in absorption has been used by Gros[1] and Slator,[2] termed "reciprocal shielding." Parallel determinations are made in thin rectangular vessels, with bilateral illumination, using a weaker solution of the absorber to shield the stronger, and conversely. Now, as the reaction itself is a direct function of the absorption of light, the concentrated solution will receive more light from the reverse side, and conversely, so that a good approximation to a homogeneous distribution of the intensity of light may be obtained.

If Beer's law hold, the fraction of light absorbed in the thickness x at a concentration c is $a = x^c$

$$i.e.\ I_x = I_0 a^x$$
$$= I_0 \mathrm{M}^{cx}$$

where M = transmission coefficient.

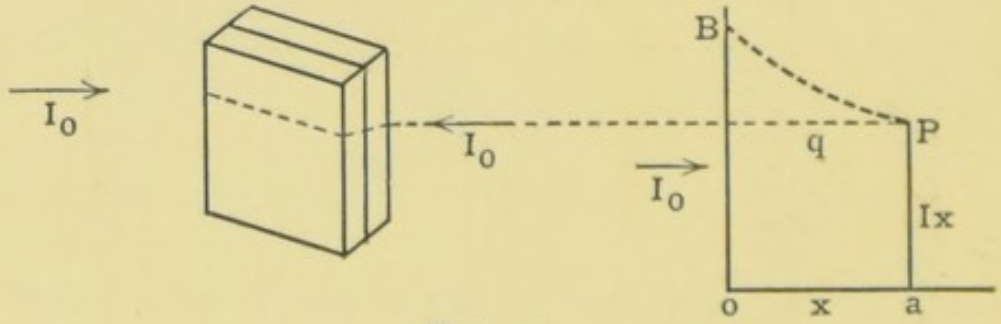


Fig. 35.

The mean light-concentration in OAPB

$$= \frac{\mathrm{OAPB}}{x} = \frac{q}{x}$$

but
$$q = \int^x I_x dx = \int^x I_0 \mathrm{M}^{cx} dx$$
$$= I_0 \left[\frac{\mathrm{M}^{cx}}{c \log \mathrm{M}} \right]_0^x = I_0 \frac{\mathrm{M}^{cx} - 1}{c \log \mathrm{M}}$$

[1] O. Gros, *Zeitschr. phys. Chem.*, **37**, 157 (1901).
[2] A. Slator, *ibid.*, **45**, 513 (1903).

Supposing we have two solutions, one of concentration c, the other $2c$ (Fig. 36).

Then in $1c$

$$I_1 = \frac{I_0 M^{cx} - 1}{c \log M} + I_0 M^{2cx} \frac{M^{cx} - 1}{c \log M}$$

$$= I_0 \frac{M^{cx} - 1}{c \log M} (1 + M^{2cx})$$

and in $2c$

$$I_2 = \frac{I_0 M^{2cx} - 1}{2c \log M} (1 + M^{cx})$$

For homogeneous distribution I should equal I_0, and so long as $M^{3cx} < 0{\cdot}5$, the deviation is very slight.

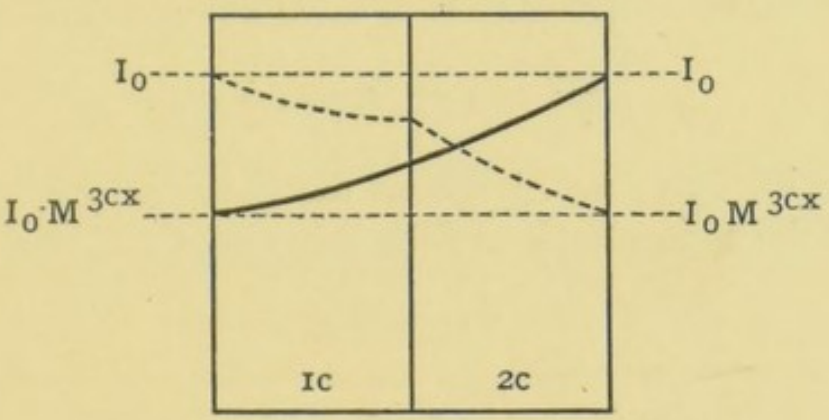


FIG. 36.

Actually it is doubtful if any photo-reaction proceeds with a higher order than 1. The velocity from Gros' formula is—

$$V = R \frac{c^{n-1} I_0}{\log M} (M^{cx} - 1)$$

Putting log M into the constant K, we have

$$-\frac{dc}{dt} = K_1 c^{n-1} I_0 (1 - M^{cx})$$

which if $n = 1$ reduces to [1]

$$-\frac{dc}{dt} = K_1 I_0 (1 - M^{cx})$$

and is identical with the form obtained on the assumption that the velocity is proportional to the light absorbed, since

$$K_1 = \frac{a}{v} \frac{\text{area of ray-bundle}}{\text{volume of illumination}}$$

[1] Cf. C. Winther, *Zeit. wiss. Phot.*, 7, 66 (1909).

On integration, $$\frac{M^{-c_t x} - 1}{M^{-c_0 x} - 1} = M \cdot K_1 I_0 t$$

c_0 and c_t are determined by analysis.

For the case of complete absorption, M^{-cx} is vanishingly small, and $K_1 I$ can then be obtained from the initial velocity.

This equation has been found to represent very well the reaction between CrO_3 and quinine in light,[1] and the decomposition of O_3 by Cl_2 in light.[2] For CrO_3 and quinine, Goldberg found for M for light of wave-length $\lambda 404\mu$

$$\text{the value } M = 10^{-30,000}$$

For a particular concentration and illumination when—

$$\frac{K I_0 a}{V} = 1{\cdot}25, \; x = 1{\cdot}6 \text{ cms.}$$

the following agreement between the observed and calculated values of the concentration of chromic acid, CrO_3, was obtained.

TABLE XV.

t in mins.	c_t found.	c_t calc.
0	41·6, 10^{-7}	41·6, 10^{-7}
200	31·4	31·4
400	20·8	21·6
600	13·2	12·8
800	7·3	6·2
1000	3·0	2·5

The above equation, which holds for any reaction in which the self-induction or auto-catalysis by a secondary reaction is small, reduces to the general monomolecular function $V = V_0(1 - e^{-Kt})$, and can be modified by a second term for auto-catalysis (self-induction).

[1] E. Goldberg, *Zeit. phys. Chem.*, **41**, 1–10 (1902).
[2] F. Weigert, *Ann. Phys.*, (4) **24**, 25 (1907).

CHAPTER VII

DYNAMICS OF PHOTO-CHEMICAL CHANGE

§ 90. Principle of Mobile Equilibrium

The examples of photo-chemical change already instanced show that we may speak of a mobile photo-chemical equilibrium in a similar specific sense that van 't Hoff used the term "mobile kinetic (thermal) equilibrium." Now, as a general conclusion from observation of the reactions between light and matter, the mobile photo-chemical equilibrium may be considered as having three principal degrees of freedom of readjustment on disturbance. In other words, it is triply indeterminate.

This adjustment may be attributed to—

(*a*) A tendency on the part of the system insolated in a field of radiant energy—the disturbing force—to become *self-luminous*.

(*b*) To become *transparent* to the insolating radiation.

(*c*) To assume a critically *reflecting condition*.

A priori, exception being made from other factors not perhaps of essential photo-chemical moment, any of these three accommodations of a photo-chemical equilibrium on variation of the energy-density of radiation incident is equally probable.

True photo-chemical equilibrium is consistent only with the co-existence of the matter of a system S in the three states indicated, hence the discussion of photo-chemical equilibrium in the abstract tends to become identical with the deduction of the laws of temperature-radiation already considered. But these laws, descriptive of the behaviour of large masses of matter composed of very many kinds of molecules, of large fluxes of radiation of every conceivable

quality and polarization, only indicate a general orientation as regards the specific behaviour of small groups of individual molecules, among which the study of photo-chemical change finds its subjects.

It is, however, certain that one possible issue to photo-chemical change, that is, to enforced disturbance of a photo-chemical equilibrium, is for part at least of the insolated matter to pass to that condition which best *reflects* the incident radiation. At the same time, remembering that light is now conceived as an electro-magnetic disturbance in a universal medium pervading matter, it should be noted that this form is likely to be a good conductor of electricity, and, as layers with metallic reflecting power are seldom or never perfect reflectors for all radiations equally, but have usually a very high absorption, amounting to extinction for a thickness of a few wave-lengths (*vide* p. 139) for certain groups of radiation,[1] this statement may also be put in the form that one highly probable issue to photo-chemical change, amounting to a permanent alteration bringing the initial reaction to a stand-still, is for the insolated material to pass to a condition of maximal reflection for one group of rays, of maximal absorption for another.[2]

For reasons which will appear shortly, it will be convenient to consider a large number of photo-chemical changes under the general head of displacements of the equilibrium—

$$S_0 \underset{\text{light}}{\rightleftharpoons} S_{-1}$$

[1] That this proposition should be generally true for the action of light on matter, whatever its state of aggregation, solid, liquid or gaseous, may appear at first improbable. But experiments on the photo-electric effect in *gases* show that it is correlated not merely with *absorption*, but with *metallic* absorption; cf. P. Lenard and C. Ramsauer, *Sitz. ber. Heidel. Akad. Wiss.*, 1911, Abh. 24, p. 5.

[2] This corresponds to a deduction made by Gibson (*Zeit. phys. Chem.* **23**, 349 (1897)) as to the general nature of photo-chemical change. But its scope is actually narrower, it only describes one form of permanent alteration or final state possible. A tendency to form bodies of increased absorption-power for active rays was postulated by W. D. Bancroft, but this also only corresponds to one phase, that of positive auto-catalysis, in photo-chemical change.

where S_0 denotes a state *transparent* to light, S_{-1} a state *opaque* to light. The production of clouds in transparent media by insolation in intense radiation corresponds to a displacement from left to right of the equilibrium schematized. On the other hand, the disintegrating effect of ultra-violet upon sundry surface-films corresponds to a displacement in the opposite sense.

It is not only the intensity and wave-length of radiation which influences photo-chemical change, but above all the duration and continuity of certain groups of rays.

§ 91. Reflecting Films and False Equilibria.

Whatever chemical change light brings about, as a permanent alteration, that which is most evident will be either of the nature of an oxidation or a reduction. These processes are of course really concomitant, but the local changes in the state of chemical combination of an element are either in one direction or the other. The most pronounced instance of optical reflecting power is shown by free metal surfaces, and the production of superficial metallic lustre is a very general resultant at interfacial planes of the interaction of light and matter. But, save when special precautions are taken to ensure such a result, it is rare that the proportion of radiant energy which is predominantly reducing in its nature is allowed full play unimpeded by radiation of a contrary character. In consequence of this, and in correspondence with the transforming effect of matter upon radiation when excited, we encounter more often than not at the surfaces of photo-chemically reactive bodies films exhibiting an alternating generation of higher and lower oxidation-stages of the same chemical elements. Thus the surface dichroism of potassium per-manganate may probably be represented chemically on the ionic hypothesis by the mobile equilibrium—

$$(MnO_4)_2'' \rightleftharpoons 2(MnO_4')$$

per-manganate manganate

a series of oscillating dissociations and associations taking

place on exposure to a heterogeneous ray-bundle. That this transition is concomitant with a change in hydrolytic equilibrium is no doubt also probable, but need not affect the above statement.

As has already been pointed out, the self-reciprocal transition (or actino-tropism) of an element from a free active condition to a *passive* state, more or less accompanied, according to the rapidity and frequency of the transition, by emission of its characteristic radiation, and its reconversion from the *passive* to the *active* state under the influence of complementary rays, is not limited to one element but is a general property of matter. Whilst the phenomenon of dichroism may be regarded as correlative with this transition for one, or more probably, in view of the reciprocal nature of all chemical change, two elements, as in the case of the manganate ion, if more than two elements are pulsating in a small region syntonically in this manner, we have the phenomenon of *pleochroism*. With complicated organic bodies an enormous variety of photo-tropic and chroma-tropic phenomena are possible.

§ 92. Second or Intermediate Condition of Equilibrium.

Equally consistent with the principle of least action is the transition of insolated matter under radiant stress to a condition of maximal *transparency* for incident rays. Whilst one set of radiations can convert *phosphorus* from the translucent yellowish phosphorus to the opaque reddish, metallic passive phosphorus, another set, specifically complementary to the first, will effect the converse change. But, for either aspect of the transition, the influence of *analytic impurities* must be taken into account, traces of other elements which act as catalysts, positive or negative, to the transition. We shall consider this again in dealing with periodicity in the phenomena of oxidation of phosphorus.

§ 93. Third Condition of Equilibrium: Luminescence.

In general, however bodies are brought thereto, light, visible and invisible, is emitted by matter in the radiant state of flame or incandescence, which is a consequence of fire or chemical interaction of the elements with great rapidity. Matter may be brought to the self-luminous condition, the furthest development of the state of photo-tonus, in a great variety of manners, some of which are dealt with here.[1]

It is not necessary, and is indeed, from the economic point of view, often undesirable, that this chemical interaction, when suspended, should imply any marked permanent chemical after-alteration in the system. That is, the chemical interaction may be iso-dynamic, all the displacements of valencies involved being virtual, or self-compensated, the nature of the radiation or disturbance propagated in the æther being a function of the virtual velocities of the interchanges of chemical affinity. Suppose again that we have a system, an ideal photo-chemical equilibrium composed of the two photo-chemically heterogeneous states S_0 and S_{-1}: that is, the intermediate phase S_0, which is relatively transparent to light, has a high dispersive power for it, but is a poor conductor of heat and electricity, *i.e.* is a good insulator, of high dielectric capacity; and what we will term the anastase S_{-1}, which is relatively opaque to light, has great reflecting power, and is a good conductor of heat and electricity. We will further suppose that in the dark, or in very weak light, the system is in equilibrium. It is evident that according as the substance S_{-1} is spatially external or internal to the substance S_0, its conductive function for heat and electricity will tend to conserve or dissipate energy stored in the system; but on the other hand, if S_{-1} form an envelope about S_0, light-energy cannot penetrate from without. We will consider the case in

[1] Beside the chapters on light-sources, and the subsequent discussion of luminescence phenomena, the following works may be referred to on the production of light and radiation:—E. C. C. Baly, *Spectroscopy*, this series; G. Urbain, *Spectrochimie*, 1911 (Paris, Hermann & fils).

which S_0 is the enveloping system to S_{-1}, and is large in proportion to the quantity of the latter.

If now such a system be exposed to light relatively intense compared with that to which its equilibrium was previously adjusted, persistent alterations of equilibrium of the system in both senses, *i.e.* from S_0 to S_{-1} and S_{-1} to S_0, may be set up. But such oscillating currents of displacement of chemical affinity, provided they are rapid enough, are equivalent to light, and such a system, passing upon insolation into such a ferment, may either—

(α) appear self-luminous in directions transverse to the insolating ray-bundle, and only during insolation. That is, it *emits* into adjacent dark or non-luminous regions;

(β) appear self-luminous in the dark on *suspense* of the exciting rays.

In the former case (α) we have the phenomenon of fluorescence, closely connected with which is the cathodo-luminescence of bodies electrically excited *in vacuo*, and the emission of X-rays and ultra-violet rays, of greater or lesser penetrating power; in the latter (β) photo-phosphorescence. They differ principally in respect to a certain impedance or time-lag, a measure of inner friction, such that in case (β) we have a storing-up of light which is not effected in (α). Hence *fluorescence* and *phosphorescence* merge imperceptibly. But this shows that another and most important condition of photo-chemical equilibrium is the self-luminous state of sources of radiation. This is par excellence the *active* state of a system, it may, reduced to the simplest terms, be regarded as produced from S_0 in proportion as its dielectric capacity breaks down. We may denote this photo-positive condition by the symbol S_1, and regard it as the katastase in the transaction. As will be indicated later in dealing with the photo-chemical processes in flames and other self-luminous bodies, the actual emission-centres appear to be electro-positively charged particles or kations. By a *katastase* then we shall understand a shell or equipotential system of such kations. The fact that elements like the halogens may also assume the self-luminous state need

not militate against this terminology, as there is a considerable amount of evidence showing that conventionally "negative" elements such as chlorine can pass into a relatively positive condition, just as "positive" elements such as copper may form part of an electro-negative group or complex anion, under appropriate conditions.

§ 94. Endo- and Exo-actinic Reactions.

Just as in thermo-chemistry we are familiar with reactions which are exo-thermic and endo-thermic, according as they are concomitant with the evolution or the absorption of heat, so we have exo-actinic and endo-actinic reactions in photo-chemistry, corresponding to the emission and absorption of light. Bodies like H_2O_2, which are the resultants of endo-thermic reaction, have a lower temperature-limit of meta-stability and an upper temperature-limit of true stability. When we consider flames as in and for themselves constituted of phases of constant composition, the fact that hydrogen peroxide and similar endo-thermic compounds, when dissociating in a labile condition between the lower meta-stable limit and the upper stable limit of temperature can initiate chemical changes similar to those produced by light,[1] such as the formation of latent developable images on silver bromide emulsions, it is evident that there is an important parallelism between thermo-chemical and photo-chemical change. This should be borne in mind when a strong contrast is drawn (see p. 51, also 384) between so-called "temperature-radiation" and chemi-luminescence. The distinction between these is not that the former is really independent of chemical changes, for the heat development in which it originates is, fundamentally, chemical reaction-heat, but that there is a thermodynamic equilibrium between the rates of change of chemical processes in opposite senses. To each level of such stationary motion of chemical affinity, in which individual and specific differences are merged in a

[1] Sometimes termed photo-echnic actions. They have been used in photography as catatypic processes; cf. J. M. Eder, *Handbuch d. Photogr.*, i. 464 (1906).

common conflux, corresponds a definite body-temperature of an insulated mass, and its correlative "black radiation." When investigating individual and specific chemi-luminescences *per se*, we are dealing with sundry isolated *factors* of "temperature-radiation." Connected with this equilibration *inter se* of the free energies of chemical reactions are two paradoxes to be dealt with more precisely later. One of these is the fact that the (apparent) body-temperature of a chemi-luminescent medium, as read with a thermometer, may be quite low, far lower than would be necessary for ordinary temperature-radiation to give visible luminosity, and the other is the fact that the visible luminosity of certain phosphors may be extinguished or quenched by infra-red rays. What distinguishes photo-chemical change from most other physico-chemical transitions is the predominant importance, so far as change of state of physical aggregation of matter is concerned, of the transition gas $\rightleftharpoons$ radiant or electrionic state, the other typical physical transitions, as liquid $\rightleftharpoons$ gas, liquid $\rightleftharpoons$ solid, being of subordinate importance photo-chemically. And we may notice that just as a mass of matter wavering between the *liquid* and the *gas* state is termed as a vapour, a mass of matter wavering between the *solid* and the *liquid* state a gel, so a *flame* may be regarded as a mass of matter fluctuating between the *gas* and the radiant or *electrionic* condition. Precisely in the fact that so far as photo-chemical equilibria proper are under consideration, we have to deal with matter and energy in a more highly differentiated and fine-grained condition, does photo-chemistry require its own system of dynamics not entirely congruent with thermo-dynamics, analogous thereto but not homologous therewith.

Sufficient has been said to show that in photo-chemical change endo-actinic and exo-actinic reactions are not phenomena which can be absolutely divided, but can be analytically discerned as complementary aspects of the same metathesis or double decomposition. In every photo-chemical change, both types of reaction occur concomitantly, just as in a sound wave the medium alternates between condensation and rarefaction.

§ 95. Photo-chemical Change in the Elements.

(i.) **Photolysis in Gaseous Systems.**—Nearly all elements obtainable in the gaseous state, when exposed to radiant energy of sufficient intensity and frequency, show characteristic oscillations between a relatively free active condition and a passive state. This phenomenon has been very extensively studied for oxygen, the activation and ozonization of which we will now consider in some detail, as it is of very far-reaching importance. The study of this and similar problems with other gases overlaps, as will be evident, with that of the behaviour of matter excited by electricity in high vacua, the phenomena which led Sir William Crookes to the postulation of a fourth or radiant state of matter, which might be said in a sense to stand to the gaseous state as this does to the liquid one, phenomena which suggest a fresh interpretation of the tag, *Satius est supervacua discere, quam nihil.*[1]

The activation of oxygen may be brought about in a variety of ways, many of which pertain rather to the study of the production of nascent elements in general than to photo-chemistry. The important ones for our purpose are : the silent electric discharge, the action of ultra-violet light, and the action of ordinary light in the presence of a specific photo-sensitizer for oxygen, an oxydase. Of these, the second one presents the photo-chemical aspect of the phenomenon in its simplest form, but it was historically anticipated by the first.

(ii.) **Ozonization by the Silent Electric Discharge.**—This is a discharge without sparking of a current of low ampèrage but high tension or potential difference between the electrodes. If one of these is drawn to a point, the discharge is termed a point-discharge, but two reciprocal surfaces may be used, usually two conaxial metal tubes, as in Berthelot's original ozonizer, and an alternating discharge passed through the gas. Warburg,[2] endeavouring to find if a relation similar to Faraday's law for the electrolysis of solutions held between the current employed and the yield of ozone, found that there

[1] Seneca, *Epistol.*, 89 *seq.*

[2] *Ann. Phys.*, [4] **13**, 464, 1904.

was a maximum yield of ozone for a particular disposition of the electrical circuit for a given velocity of convection of the oxygen stream, and which maximum was not exceeded by further increase of current. He concluded that ozonization was due to ultra-violet light, and that a stationary value was reached when the ozonizing and de-ozonizing forces in this were equilibrated.

These results were confirmed by A. W. Gray.[1] The opinion that oxygen can exist in both an active unsaturated condition and a passive saturated condition,[2] has long been prevalent in connection with the phenomena of autoxidation. Schönbein in particular[3] brought forward a photo-chemical theory to explain this alternation of state, according to which the activation was due to light. At the same time he suggested that oxygen excited by light would have an increased affinity for hydrogen.

So far as the direct action of light on oxygen is concerned, it is evident that the rays must lie beyond $\lambda = 200\ \mu\mu$, which is the limit at which air begins to show a powerful absorption.[4]

Physically speaking, this absorption results in an ionization of the gas, but this does not entirely cover the chemistry of the process. It was shown by Lenard[5] that very short ultra-violet light ozonized oxygen, that is, brought about the reaction

$$3O_2 = 2O_3.$$

Nernst[6] as well as Warburg[7] expressed the opinion that the action of the silent discharge upon oxygen and other gases

[1] *Ann. Phys.*, [4] **13**, 477 (1904).

[2] Cf. J. W. Mellor, *Chemical Statics and Dynamics*, this series, p. 307.

[3] *Journ. prakt. Chem.*, **75**, 99 (1858); **77**, 69 (1859); **78**, 69 (1859); **79**, 87 (1860); **93**, 25 (1864); **105**, 226 (1868). Note that the essential fact of autoxidation as presented by Schönbein is that the binding of one portion of oxygen in a passive form is irreducibly concomitant with loose fixation of an equal portion in the active form, *i.e.* the proportions synergically rendered *active* and *passive* are equal.

[4] Cf. E. C. C. Baly, *Spectroscopy*, this series, p. 258.

[5] P. Lenard, *Ann. Phys.*, [4] 1, 486, 403 (1900).

[6] *Ber. deutsch. electrochem. Ges.*, 1894, p. 38.

[7] *Loc. cit.*, p. 253.

was essentially photo-chemical. Goldstein,[1] using the discharge in a Plücker tube with a quartz window, found that the air was ozonized near the quartz. The action was still more intense within the tube.

(iii.) **Ozonization by Spark Discharge.**—Regener[2] made a quantitative study of the influence of ultra-violet light from a spark upon oxygen.

At the source, a spark discharged was passed between aluminium electrodes enclosed in a quartz tube. Sealed on to this as a jacket was a quartz vessel into which oxygen was introduced. The heated gases from the spark were constantly

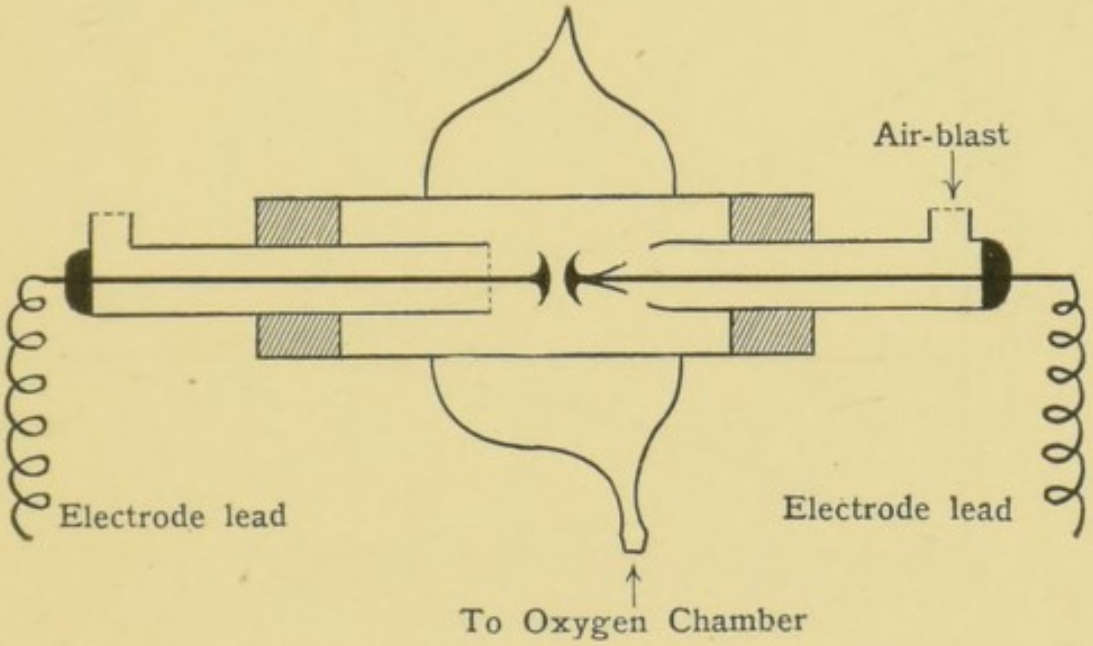


FIG. 37.

removed by an air blast so that the temperature did not rise and induce the thermal decomposition of ozone. The disposition of the apparatus is shown in the diagram (Fig. 37).

Experiment showed that on introducing purified oxygen into the outer jacket, the ozone reached a constant maximum percentage, about 2 per cent. actually, whilst if gas containing a higher percentage than this was introduced, the ozone value fell to the same level. This installation of photo-chemical equilibrium is shown in the diagram (Fig. 38).

[1] *Ber. d. deutsch. Chem. Ges.*, **36**, 3042 (1903).
[2] *Ann. Phys.*, [4] 20, 1033 (1906).

Hence a stationary value under given experimental conditions, similar to the polymerization of anthracene, is obtained, dependent upon equilibration of ozonizing and de-ozonizing rays.

(iv.) **The Spectral Locus of the Active Rays.**—The rays producing ozone must be of very short wave-length. Kreusler[1] has shown that oxygen begins to absorb perceptibly at about $\lambda = 193\ \mu\mu$, the absorption then increasing rapidly. Schumann found that a layer 1 mm. thick at a pressure of 760 mm. mercury entirely absorbs rays beyond $170\ \mu\mu$, so that though the range

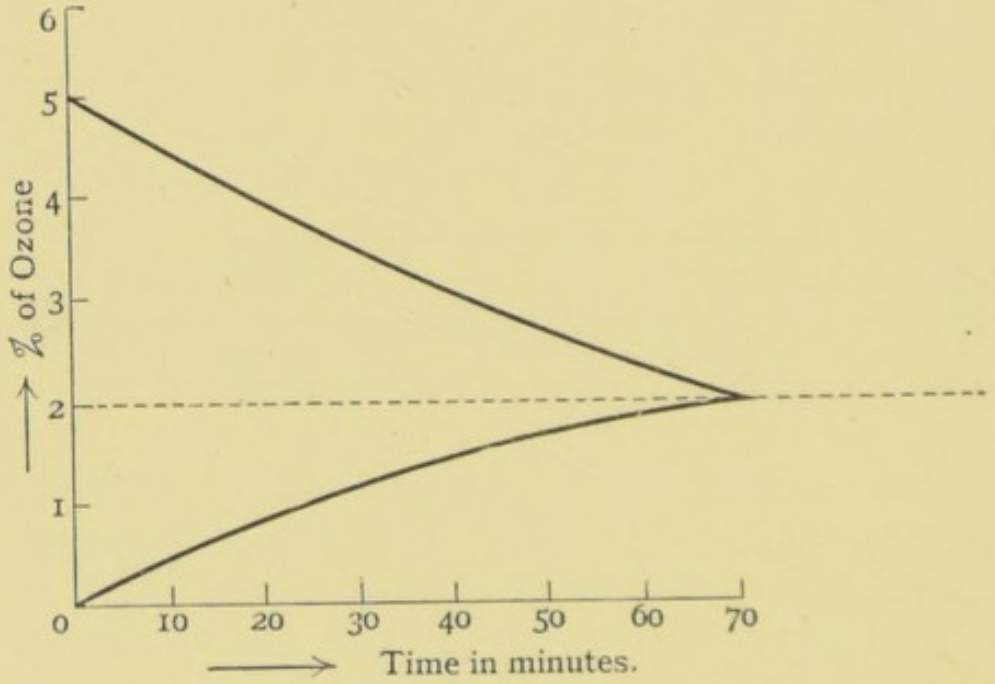


FIG. 38.

of the activating rays is somewhat uncertain, its lower limit is known, whilst its maximum is perhaps about 100 to 200 $\mu\mu$, supposing, as seems probable from the greater difficulty met in activating nitrogen, that an upper limit also exists, *i.e.* that beyond a certain value of diminishing wave-length of radiation, oxygen would again become unaffected.

The de-ozonizing ultra-violet rays would seem to lie in the ultra-violet absorption spectrum of ozone, which has been measured by E. Meyer.[2] He determined the absorption-

[1] *Ann. Phys.*, **6**, 419 (1901).
[2] *Ann Phys.*, [4] **12**, 855 (1903).

coefficients for different wave-lengths in the band, and gives the following values :—

The absorption-coefficient α was calculated from the expression $I = I_0 10^{-\alpha d}$, for $d = 1$ cm. of purified ozone at 0° C. and 760 mm. mercury.

He gives the following values :—

TABLE XVI.

λ	α	λ	α
185 μμ	—	250 μμ	123
193	11·7	260	126
200	7·8	270	116
210	11·5	280	73·4
220	19·2	290	38·6
230	48·6	300	30·3
240	105·0		

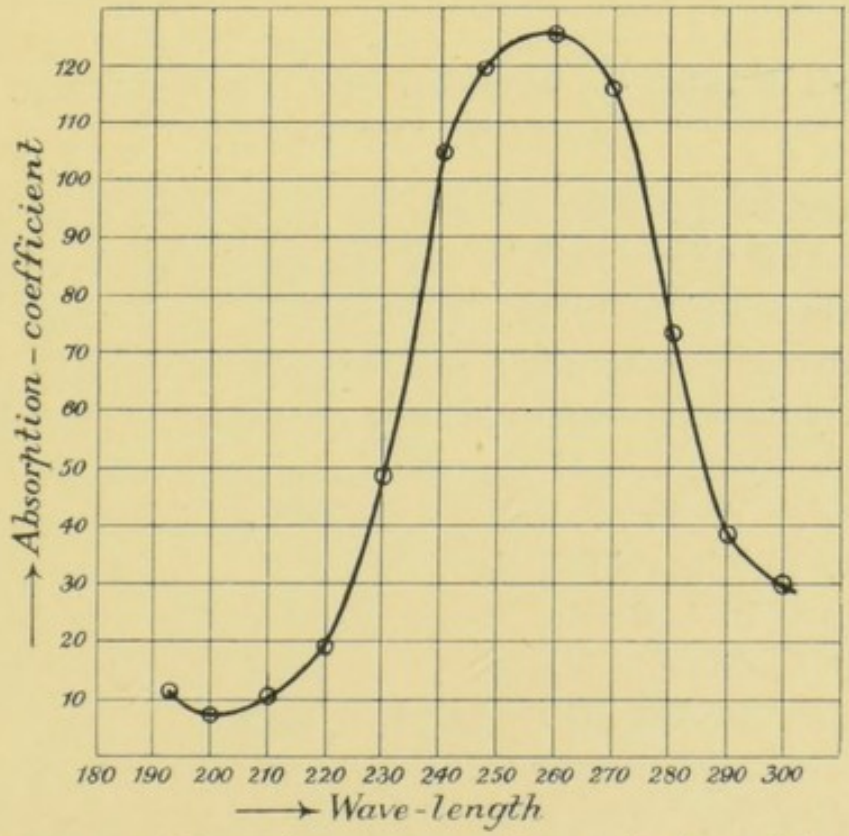


FIG. 39.—Absorption-spectrum of ozone in ultra-violet.

The band commencing at $\lambda = 200$ μμ is no doubt the oxygen-band already referred to. Hence the stability of

ozone is a function both of the active mass of oxygen and the density of ultra-violet light beyond 180 $\mu\mu$.

(v.) **The Thermal Counter-effect.**—Not only do ultra-violet rays of a certain span decompose ozone, but this counter-effect is also brought about by heat. Regener found that an elevation of the temperature from 20° C. to 54° C. lowered in a certain experiment the equilibrium-yield from 3·4 per cent. to 2·7 per cent. Now it is known that beside the band in the ultra-violet, ozone has an absorption-strip in the infra-red region, first mapped by Ångström, with a maximum at about $\lambda = 1040$ $\mu\mu$. This maximum, which corresponds of course also to a second maximum, expresses the dispersion-power of ozone for radiant energy. The actino-tropism[1] of the element oxygen, which is the energetic concomitant of its allotropy or dynamic isomerism, is therefore a doubly periodic function of the wave-length[2] and intensity of the radiation it finds itself in.

§ 96. Chemical Actinometry, particularly of Ultra-violet Light.

It may be pointed out at this stage that chemical actinometry and the dynamics of photo-chemical change are necessarily complementary. Every photo-sensitive reaction can furnish an actinometer for a specific group of radiations, whilst conversely the actinometer is only quantitatively reliable in so far as the dynamics of the transition made use of are comprehended. We have already discussed the important reaction of *oxygen* to ultra-violet light, a reaction important meterologically and biologically, as well as chemically, and we will continue with further consideration of the action of ultra-violet light of various wave-lengths upon gases, premising that the silent electric discharge may be considered as one source of short-wave radiations. This step is the more consequent with the

[1] This somewhat cumbrous expression is used to denote the general behaviour of an element in regard to radiation over its cycles.

[2] Or inversely, of oscillation-frequency.

general influence of radiation on matter, in that it corresponds to the processes taking place in the upper atmosphere of the earth under the sun's rays. That not only oxygen and hydrochloric acid gas mixture,[1] but also other gases are susceptible of alteration by light, provided the vibrations are of sufficiently high oscillation-frequency, was shown by P. Lenard, who indicated that at the same time the gas is dissociated electrolytically into negative and positive ions—the latter in part of considerable magnitude—but that *mist* or light-cloud formation of electrically neutral liquidogenic droplets is also effected, and this not necessarily by the adventitious co-working of solid bodies, but simply through the action of the periodic electro-magnetic forces of the light. The continuation of these experiments has resulted in the elaboration of a very powerful source of ultra-violet rays of very short wave-length, the electric spark from an induction coil between metallic electrodes, great attention being paid to the secondary spool as regards insulation. The capacity could be increased with plate-condensers, and an electrolytic interruptor was used, with a platinum electrode for current up to 60 amps., a nickel electrode for greater currents.

An earthenware vessel of some 60 litres volume was used with these high loads, to avoid excessive heating of the fluid in the interruptor. Details of the electrical constants of the light-source are given in the paper referred to.[1] It was calculated that the energy-consumption in the sparks per second was about 900 volt-coulombs. This corresponds approximately to the consumption for an arc-lamp of moderate strength (20 amps. at 45 volts tension of the carbons). But the nature of the consumption is essentially different. In the arc-lamp this is equally distributed over the whole duration of a second, but in the spark it is concentrated in small fractions of a second, interrupted by relatively large pauses. The number of oscillations (in the alternating circuit) was calculated to be less than 50, and as in each oscillation only $\frac{1}{4}$ period can be reckoned as light-productive current, it follows that the effective time per second is less than $53 \times 50 \times \frac{1}{4} \times 10^{-6}$ secs.

[1] *Chlorknall-gas*, or chlorine-hydrogen detonation mixture.

= 0·0006 sec. Hence the impulse afforded is, for the conditions described, more than 1000 times as great as with the arc.

The details are given to illustrate the importance of the duration and concentration of energy in light-sources as affecting the nature of the emission. It is a point of equal importance for spectroscopy and photochemistry.

The photo-electric effect or ionization of gas by radiation will be dealt with later; we will continue for the present the consideration of the chemical action of light on gases.

It is evident, on consideration of the scale of oscillation frequencies of radiant energy, or, reciprocally, of wave-lengths, that the ultra-violet spectrum, limited on this side by the visible spectrum, is theoretically indefinite in extent on the further side. Practically, we know of ultra-violet light up to about 100 $\mu\mu$.[1] It is convenient to have some notion of the rougher group-division of ultra-violet light, something crudely corresponding to the division of the visible spectrum into colours, and a provisional tabulation of the kind is given. It is quite time that the indefinite usage of the term "ultra-violet light," without qualification as to the *nuance*, was abandoned. The table following is due to P. Lenard and C. Ramsauer,[2] and the rough division of the spectrum and the nomenclature for the groups, although more or less arbitrary, suggests what is required.

[1] "The actions of ultra-violet light of very short wave-length on gases, and a very powerful source of this light," P. Lenard and C. Ramsauer, *Sitz. ber. d. Heidelberg. Akad. d. Wissenschaften*, 1910, sect. 28, pp. 1–20. For important investigations on the spark-discharge, see A. Schuster and G. Hemsalech, *Phil. Trans.*, A. **193**, 189 (1899), and G. Hemsalech, *C.R.*, **25**, June (1906).

[2] P. Lenard and C. Ramsauer, *Sitz. ber. d. Heidelberg, Akad. d. Wiss.*, Abh. **31**, 1910, p. 35.

TABLE XVII.

REGIONAL DIVISION OF ULTRA-VIOLET RAYS.

Region of wave-lengths in $\mu\mu$.	Denomination (or abbreviated denomination).	Remarks on characteristics and sources.
500–440	Blue	Visible
440–380	Violet	Visible
380–340	Glass-ultra-violet (Glass-violet)	Transmitted by ordinary glass in moderately thick layers; profusely emitted by electric arc with carbon poles.
340–300	Jena-glass-ultra-violet (Jena-glass-violet)	Transmitted by Jena ultra-violet-crown glass; profusely emitted by uviol mercury lamp
300–220	Quartz-glass u. v. g. (Quartz-glass-violet)	Transmitted by *fused* quartz (and calc-spar) in not too thick layers; the last portion of the emission of quartz-mercury and quartz-amalgam lamps
220–180	Quartz-crystal u. v. (Crystal-violet)	Transmitted by moderately thick layers of crystalline quartz (also by gypsum and rock-salt) can be decomposed in the quartz spectrograph
180–120	Fluorspar u. v. (Schumann violet)	Still transmitted by good fluorspar, but completely absorbed by short air-spaces; decomposed in vacuum spectrum apparatus with fluorspar media
120–90 (?)	Reflex-u. v. (reflex-violet)	Strongly metallically reflected from all the above-mentioned solid media, according to theory of dispersion only to be investigated in their absence; dispersable with reflection-grating (Lyman)
Shorter waves	Trans-reflex-violet	Incognita

§ 97. Photo-chemical Reactions in Gases and Vapours

The action of ultra-violet rays (spark-discharge or silent electric discharge) on gases has been much studied of late. It is obvious that the greatest activity is initiated in the medium when the spark-discharge is passed directly through it, without the intervention of absorbing layers. On the other hand, although this implies the most rapid communication of energy to the medium, it is not necessarily the most economic process in regard to yield of a particular product, unless effective means are taken to remove this as soon as formed from the region of equilibrium, the danger zone in which it is created and in which, in virtue of the reversibility of the reaction (usually by the consequent thermal counter-oxidation), it is liable to decompose, regenerating the initial substance or substances.

This holds true for all photo-chemical changes, and conditions the usual practice of sensitizing the reaction in the desired direction by such means as an absorbent for the reaction product, due regard being paid to the adjustment of feed of initial material to the energy-load, peripheral cooling of the reaction chamber, or rapid cooling of the product as swept out of the zone of change. It is essential to distinguish this *contingent* sensitizing (or economizing), of a reaction itself directly light-sensitive, from *effectual* sensitizing of a reaction not itself directly sensitive to a certain kind of light by coupling it with small quantities of a system which is directly sensitive to these, and which communicates the impulsion to the other, possibly by emitting, in course of one period of its own cycle, radiation by which the other is affected. A convenient apparatus for the study of the action of ultra-violet light on gases is described in the section on photo-electric effects, because the accessory conserving and measuring part consists of electric fields and charged (statically charged) plates to which positive and negative conductors are drawn and quantitatively determined.

It must be remarked again that the action of radiant energy in all the reactions detailed cannot be declared as *per se* either dissociating or associating (synthetic), seeing that great numbers of syntheses are effected concomitantly with decompositions. But, in order that a realizable and permanent alteration of chemical equilibrium may be effected by light, we can but conceive that the valencies of the reacting substance are loosened and perturbed, and that consequent with this enhancement of the inner degrees of freedom of the system, the opportunity is given for new combinations to occur at the expense of those terminated. It seems very probable that in the case of compound atoms, or molecules, disjunction into single atoms may be temporarily effected, and this may be followed by recombinations in modified configurations, or, where different elements are present, new synthetic products.[1] This is particularly the case in the action of light on organic compounds, in which the peculiar perturbations initiated by light induce immediately recombinations of the atoms, or inter-molecular rearrangements of the atoms, to complex compounds only to be formed by very laborious and roundabout methods in the ordinary laboratory practice. It is somewhat as if a certain nascent state of the elements, a period in their cycles when their elective affinities are least suspended, is induced *integrally*, in one operation, in such photo-chemical changes, which has to be performed step by step in ordinary practice. The problem which vegetative life solves, of restoring inorganic matter to the animate world, is accomplished by a chemistry

[1] A further refinement of the mechanism of this dislocation is offered by the electron theory. According to this, either the initiation or the cessation of a stream of electrons in a wire causes an ether-wave. Conversely, an ether-wave may start or stop such a stream. On the same theory, chemical affinity, *i.e.* chemical potential energy, consists in the rotational energy of satellite electrons about a central atom; valency depending on the *numerics* of the satellite system. This rotation can be started or stopped by an ether-wave of appropriate wave-length. Such waves, as u.v. light, may therefore alter the *numerics* of the rotational systems, and bring about immediate readjustments between the atoms.

sui generis which has the closed affiliation with photo-chemistry.

By the use of the silent electric discharge S. M. Losanitch[1] brought about the following reactions, for which the concomitance of dissociation and condensation changes is obvious.

Substance.	Product.	Remarks.
$4SO_2 \rightarrow$	$2SO_3 + S_2$	
$4NO_2 \rightarrow$	$N_2O_3 + N_2 + O_2$	A certain amount of ozone also formed
$m(CS_2) \rightarrow$	$(CS_2)_m$	
$3CS_2 + H_2 \rightarrow$	$C_3H_2S_6$	
$3CS_2 + H_2S \rightarrow$	$C_3H_2S_6 + S$	The sulphur re-aggregated
$3CS_2 + 2CO \rightarrow$	$3CS_2 . 2CO$	
$C_2H_2 \rightarrow$	$C_{48} . H_{46} + H_2$	Insoluble body which decomposes at 100° C. Shows a species of radio-activity, discharging an electroscope
[2] $C_2H_4 \rightarrow$	$C_{30}H_{54} + 3H_2$	
$C_2H_2 \rightarrow$	$C_{20}H_{26}$ (ca)	Other hydrocarbons of lower weight also produced

Brodie[3] showed that in the electric discharge CO_2 was decomposed to CO and oxygen, the latter passing to ozone. The formation of condensation-nuclei in CO_2 by ultra-violet light has been studied by Lenard and his co-workers.[4] When ultra-violet light is propagated through water-vapour, it appears that hydrogen-peroxide may be formed, in agreement with the reversible reaction

$$2H_2O \text{ (or } H_4O_2) \rightleftharpoons H_2O_2 + H_2.$$

[1] *Ber.*, **40**, 4656 (1907).

[2] Z. Jowitschitsch, *Monatsheft.*, **291**, 14.

[3] B. Brodie, *Phil. Trans.*, **164**, 83 (1874). The action was greatest with dried gas, water-vapour impeding the decomposition. Similar results were obtained by Chapman (*Trans. Chem. Soc.*, **91**, 942 (1907)).

[4] P. Lenard and C. Ramsauer, "Formation of condensation-nuclei by light in the atmosphere of the earth and in other gases." *Sitz. ber. d. Heidelberg, Akad. d. Wiss.*, Abh. **16**, p. 23 (1911).

Thus the production of H_2O_2 was impeded by excess of hydrogen.[1] It has been shown that certain ultra-violet rays can decompose water-vapour into oxygen and hydrogen.[2]

On passing the rays through air, E. Warburg and G. Leithauser[3] found that N_2O_5 is produced, together with traces of an unknown compound of oxygen and nitrogen. Correlative to this Regener[4] found that NO, NO_2, and NH_3 are decomposed.

With regard to ammonia vapour in air, we have the following reactions occurring under the ultra-violet excitation—

$$\begin{matrix} NH_3O_3 \\ NH_3 \end{matrix} \rightleftharpoons NH_4 . NO_3 + H_2$$

$$\begin{matrix} NH_3O_3 \\ NH_3O_3 \end{matrix} \rightleftharpoons NH_4 . NO_2 + H_2O + O_2$$

which are reversible, the salts being subject to thermal decomposition. Experiment goes to show that the activation of *nitrogen per se* is only difficultly effected by very narrow groups of ultra-violet rays. The use of the high-tension arc for the production of atmospheric nitric acid may be noticed in this connection.[5]

All these reactions are at least partially reversible, the conditions of equilibrium being similar to those discussed under ozonization. A. Coehn and H. Becker[6] have determined the equilibrium for the reaction—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

which gives stationary values depending on the intensity of light. The value of the constant

$$K_{light} = \frac{[O_2] \times [SO_2]^2}{[SO_3]^2}$$

[1] C. T. R. Wilson, *Phil. Trans.*, **192**, 412 (1899); P. Lenard and C. Ramsauer, "Actions of ultra-violet light of very short wave-length on gases." *Sitz. ber. d. Heidelberg, Akad. d. Wiss.*, Abh. **31**, 11 (1910).

[2] A. Coehn and A. Becker, *Zeit. phys. Chem.*, **70**, 88 (1909).

[3] *Sitz. ber. Berl. Akad.*, 229 (1907).

[4] Cf. M. le Blanc, *Zeitschr. Elektrochem.*, **14**, 361 (1908).

[5] G. Brio, *Phys. Zeitschr.*, **8**, 792 (1907).

[6] *Zeitschr. physik. Chem.*, **70**, 88 (1910).

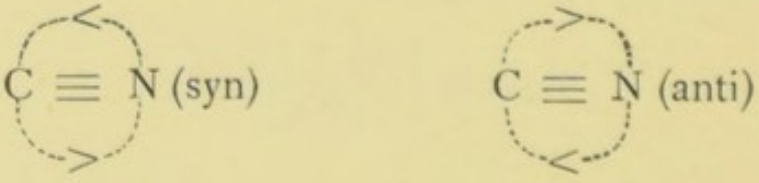
is independent of the temperature between 20° C. and 800° C. For the temperature-coefficient of the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

between 50° and 160° the value 1·2 per 10° C. was obtained. Taken in conjunction with the independence of K, the equilibrium-constant $= \frac{K_1}{K_2}$, this indicates that the converse reaction has a negative temperature-coefficient over a certain range.[1]

D. Berthelot and H. Gaudechon [2] have shown that the mercury-quartz ultra-violet light effects decomposition of alcohols, aldehydes, organic acids, and ketones, followed by condensations.

The same investigators found that cyanogen, illuminated with ultra-violet light in the presence of oxygen, gives para-cyanogen $(CN)_n$, CO_2, and nitrogen. As will be noticed in connection with the formation of condensation-nuclei (apparently *solid* particles, or dust, formed in a gas or vapour, which then induce the deposition of a saturated vapour present as mist and cloud) the polymerization of cyanogen is only one example of many such changes. It seems very probable that in such cases a closed grouping of many identical molecules takes place about a single atom of another element, very often oxygen. In the case of para-cyanogen, we might represent a cross-section through the nucleus by such a closed conformation or compenetration of ellipsoids, representing each a



[1] The dielectric constant or specific inductive capacity of many solid dielectrics has a negative temperature coefficient above a certain temperature, *i.e.* they break up, or their insulating power breaks down at high temperatures.

[2] *C. R.*, **150**, 1327 (1910). A general review of the photo-chemical activities of the silent discharge is given by E. Warburg in the *Jahrbuch. d. Radioaktivität*, **6**, 181 (1909).

half-molecule in internally compensated conjugation, the half-molecules of $(CN)_2$ differing according to the direction of rotation or circulation of the quasi-free residual affinity. If we suppose the compenetrating ellipsoids (represented *in plano* by elliptic sections) to form a self-closed shell about a meta-centre, conceivably a trace of another element,[1] and to compenetrate so that conjugate foci of alternate ellipsoids coincide, we have a crude image of the possible structure (in compenetrating atomic electro-magnetic fields) of a persistent nucleus in photo-chemical change, a confocal homœoid or

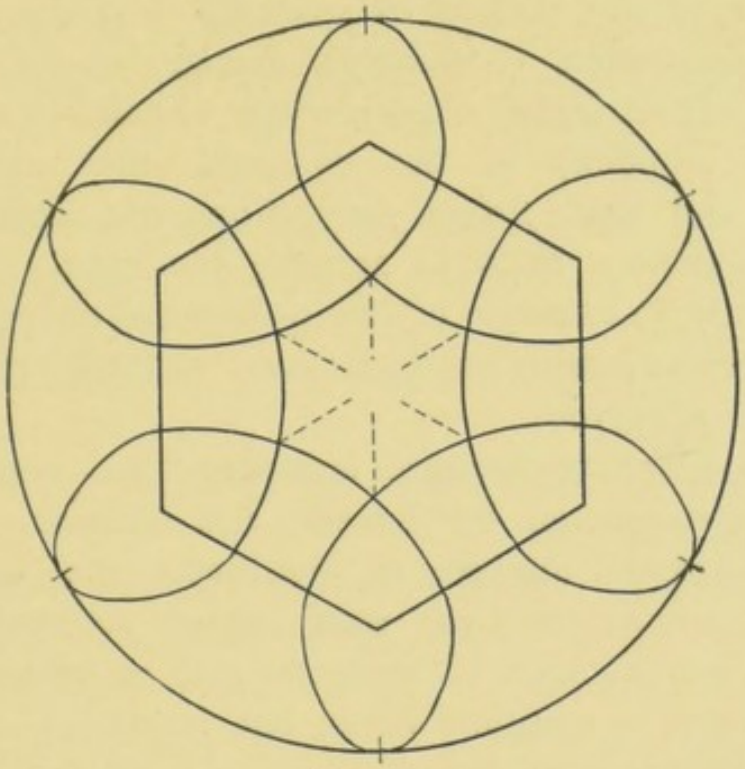


FIG. 40.

luminophore. As we shall see, such ferments play a large part in this science, being quite neutral (passive) so long as the residual affinities of the enveloping system are entirely centripetally engaged with the meta-centre, but even so capable of variable expansion and contraction, retaining the same relative configuration with respect to the centre and auto-catalytically influencing, in consequence with this rhythm,

[1] It is not necessary to suppose that there is more than a *trace* of the other element; a single atom of this circulating at great speed could feasibly effect the persistence of several such shells about its path.

chemical changes in matter interstitial to the expanded shell; *i.e.* pseudo-reversible changes similar to the *setting* and *swelling* of *gels*.

§ 98. The Problem of Photo-Chemical Induction.

The variety of the reactions in gases effected by the radiant energy in the invisible spectrum (ultra-violet rays), taken in conjunction with the fact that such radiation, though less in intensity and duration as the effective disturbance is less rapid and smaller, is not limited to sparking discharges, but is a universal concomitant of chemical change, would lead us in advance to expect highly characteristic anomalies and deviations from simplicity in the dynamics and energetics of photolysis, and that, *primâ facie*, from the interference of alien components. Such is actually the case. Practically there is hardly an example of photo-chemical change in which the phenomenon known as "induction" or initial perturbation has not been observed.

The name "photo-chemical induction" was applied to the following phenomenon by Bunsen and Roscoe. Using a specially prepared mixture of hydrogen and chlorine in equivalent proportions over water as an actinometer, they found that on exposure to light the rate of change did not at once assume a constant value, but increased at first and then attained a steady value, at which it remained so long as the exposure was continued. On cutting off the exposure, leaving the mixture unilluminated (dark period) for some time, then re-exposing, it was found that the same phenomenon recurred, so that, whatever the nature of the reaction-mixture for the period of constant velocity of change (we shall term this the period of *photo-tonus*), there had been a deduction or declension from it requiring a fresh photo-chemical induction. The following table illustrates the induction effect[1]:—

[1] "Photochem. Untersuch.," Ostwald's *Klassiker*, **34**, 363; *Pogg. Ann.*, **100**, 481–516 (1855).

TABLE XVIII.

Time in mins.	Scale-readings.	$\frac{\Delta x}{\Delta t}$.
0	100	—
1	100·5	0·5
2	102·1	1·6
3	102·6	0·5
4	103·2	0·6
5	105·3	2·1
6	119·9	14·6
7	139·1	29·2
8	170·2	31·1
9	200·6	30·4

It is entirely congruent with the virtual reversibility of photo-chemical reactions that the phenomena of induction (and deduction) have been remarked in some measure in practically every one studied. But the number submitted to accurate kinetic investigation is yet small, and it is possible by suitable experimental precautions to make the induction period extremely short. As we shall see, it is not so much inherent in the nature of chemical change itself, which can proceed with velocity equal to or greater than that of light, but rather in a variety of mechanical hindrances corresponding to the interference of simple independent reactions, resulting in an apparent retardation of the rate of change. An example of a reaction in which preliminary precautions secured a practical abolition of this induction has already been given, in the case of $2HI + \frac{1}{2}O_2$ studied by Luther and Plotnikoff (p. 232), but by far the most searching inquiry into the origin of the phenomenon has been made by Chapman and Burgess, whose work on "negative catalysis" in relation to the union of hydrogen and chlorine in light will be discussed immediately. The following table gives the more prominent photo-chemical reactions in which "induction" was encountered :—

TABLE XIX.

Reaction-mixture.	Studied by
$H_2 + Cl_2$ in light	Bunsen and Roscoe.
$CO + Cl_2$,, ...	M. Wildermann.
$H_2O + Cl_2$,, ...	Wittwer.
$Cl_2 + C_6H_6$,, ...	Slator, Goldberg.
$Br_2 + \begin{cases} C_6H_6 \text{ ,, } \\ \text{homologues} \end{cases}$	Various.
$Cl_2 + C_2H_2$ in light	Römer.
$Cl_2 + C_4H_4$ COOH | ,, ... COOH	Eder.
$HgC_2O_4 + (NH_4)_2C_2O_4$	
Formation of photo-electric cells, photo-electric effects with metals, sulphides and halides	Becquerel, Wildermann and others.
Formation of latent images with silver halides and photographic preparations.	Various.

Of these, the union of hydrogen and chlorine in light has long been the favourite joust in the photo-chemical lists, and recent investigations have contributed very considerably to our knowledge of the mechanism of the reaction.

In essentials, the method consists in exposing a mixture, in nearly equivalent proportions, of gaseous hydrogen and chlorine over water to light in shallow vessels. The water is continued in a column provided with a scale, and as the soluble hydrochloric acid is dissolved in the water, the contractions of the column enable the rate of reaction to be followed.

§ 99. DEPENDENCE OF INDUCTION—PHENOMENA ON THE MANNER OF PREPARATION OF THE MIXTURE.

Bunsen and Roscoe's experiments on the induction period in light with hydrogen-chlorine mixtures showed that this period was very sensibly affected by any modification of the preparatory process, and in particular by contamination of the

gases by foreign substances. They endeavoured to ensure purity of the gases both in the original preparation (by electrolysis of aqueous hydrochloric acid) and in the actinometer by washing out all parts beforehand with a current of the electrolytic gas. By these precautions they could abbreviate the induction, but not entirely remove it. The next important work on the process, subsequent to Bunsen and Roscoe's, was done by E. Pringsheim.[1] This investigator did not agree that there was sufficient reason to postulate a specific "photochemical extinction" of light by the actual union of hydrogen and chlorine, differing from the "optical" and "thermal" absorptions of light in the mixture. He considered that, according as union was effected or not, the partition of the energy of the system between kinetic (translatory) and potential (rotational) energies would be different in the two cases.

In the kinetics of the reaction course he distinguishes three sub-periods—

(*a*) Total suspense, no perceptible formation of acid; (*b*) period of varying velocity (acceleration) of change; (*c*) steady period of constant velocity.

§ 100. Theories on Induction and Deduction.

A comparison is often drawn between the velocity of a chemical change and the current in an electric circuit. The current, which is the rate of flow of electricity through a conductor is, as is well known, given for a single simple circuit, in which the current is continuous and steady, by Ohm's law. $C = \frac{E}{R}$, where E is the electro-motive force taken round the circuit and R is its resistance. But a chemical system, such as a mixture of H_2 and Cl_2, is, as in equilibrium, a closed circuit, or rather a system of closed circuits insulated in a medium of definite specific inductive capacity, *e.g.* water-vapour, if air, etc., be excluded. One would anticipate, therefore, that on changing the flux of

[1] E. Pringsheim, *Ann. Phys.*, **27**, 384 (1887).

force through the system, by means of an inducing or primary circuit, videlicet the light-source, that some phenomenon, analogous to the induction currents discovered by Faraday in a secondary circuit parallel to the primary, would occur.

Now although the phenomenon of chemical induction in the case of H_2/Cl_2 mixture is sometimes said to be different from the *recognized* cases of sympathetic or coupled chemical changes,[1] for which Kessler proposed the term idio-chemical induction, there is no doubt that the two merge imperceptibly. This will be the more apparent when we consider the further analysis of photo-halogenizations, especially with chlorine. The essential phenomenon of idio-chemical induction is that a slow reaction between, say, A and B, is accelerated by a simultaneous rapid reaction between A and C. It is desirable, in order that the completest generality be given to the statement, to state that a reaction of *variable* velocity between A and B is regulated (*i.e.* either accelerated or retarded) by a simultaneous reaction between A and C. If, possibly owing to accessory circumstances not inherent in its nature, the reaction between A and C (the *rapid* reaction) is the faster, it is termed the primary change, the slower change is termed the secondary. The substance taking part in both is called the *actor;* that reacting with it in the primary, the *inductor;* and that reacting with it in the secondary reaction, the *acceptor*. This disposition then has considerable analogy with that of the mechanism of induced electro-dynamic currents. Evidently the problem becomes more complex if this interference is extended, so that neither B nor C are unambiguously limited to reaction with A. Both in practice and theory, it becomes desirable, from an economic standpoint, to reduce such a possibility to a minimum, and this can be effected actually by coupling the *primary* or *primitive* reaction, of A and C with a *force majeure*, an *inprimitive action* which can be reckoned as constant and independent, for the observable periods, of the *primitive* and *secondary* reactions. An example will make this clear. Suppose the rapid reaction of C with A to be the chemical change *in* a light-source,

[1] *Pogg. Ann.*, **119**, 218 (1863).

the slow reaction of A with B to be an induced photo-chemical change. Then the *inprimitive action* is the power controlling the working of the light-source, independently of its induction of the reaction between B and A. Under such a condition, we study photo-chemical equilibrium reduced to its simplest terms, so far as heterochemical change, between different elements is concerned, but we have to deal very definitely with the nature of the process *in* the light-source. Now suppose that the light-source itself may be regarded as *inprimitive*, and affecting the mutual induction of the reactions of A with B and of A with C. We shall find that one possibility is that the side-reaction or secondary reaction may so control the primary that the reaction in this takes place with a *finite* velocity instead of with an *infinite* velocity. The proof of this would be furnished if, on reducing the possible influence of B to a minimum, the primary reaction took place with a velocity approaching infinity, that is virtually, with the speed, *ex hypothesi* infinite, of the inprimitive process.

We shall see that this case has been experimentally realized for the reaction between hydrogen and chlorine, in which the influence of third components was made *nil*. In this case it is a matter of convention whether the third component be termed the *acceptor* or the *inductor*, the terms become interchangeable. In the case referred to, the investigators termed the third component the inhibitory substance or inhibitor.[1] The analogy between electro-magnetic induction-currents and photo-chemical changes may be regarded as firmly established, both from the experimental parallels which can be drawn, and from the electro-magnetic theory of light.

The phenomena of the mobile photo-chemical equilibrium correspond closely with Lenz's law for induced currents : *the direction of an induced current is always such that by its electro-magnetic action it tends to oppose the displacement.* This holds for *variation* in the strength of a current, which produces in the circuit through which it passes an induction current superposed on the principal current, and opposing the actual

[1] D. L. Chapman and P. S. MacMahon, *Trans. Chem. Soc.*, **97**, II. 845 (1910).

variation of strength, tending to diminish one which is increasing and increase one which is diminishing. That is, this *variation*, the induction of a current on itself (which may be, *primâ facie*, positive or negative), which is termed self-induction, gives rise to an *extra* current. If we consider that the atoms of chemical elements are, electrically speaking, self-closed circuits of electro-magnetic forces, which, according to some, possibly periodic, function, vary between a conducting and an insulating condition, so that the atoms of the same element may on occasion attract each other, on occasion repel each other, we should expect to find useful analogies, for quantitative purposes, between the variation of this idio-chemical affinity, or residual affinity, and the variation of observable electric currents.

Whilst Ohm's law is a necessary and sufficient expression for any simple self-closed circuit traversed by a continuous current, the expression for a complex circuit, with variable self-induction and capacities of several sub-circuits assumes a more complicated form.

In any circuit, the total flux of force is proportional to the current, and may be expressed by

$$F = S.C$$

where S is a factor dependent upon the actual geometrical and other dispositions of the circuit, and is the coefficient of self-induction. It is a quantity of the same kind as the coefficient of mutual induction of two circuits. In the case of any variation of the current, the self-induction gives rise to an E.M.F. tending to oppose the variation, chemically speaking, to a reflex liberation of affinity contra-valent to the first transient variation, and which we can express either inversely, by $\epsilon = \frac{W}{C}$, where W is the work done in unit time as the result of a current of strength C, or, directly, in terms of its generating function F, as $\epsilon = -\frac{dF}{dt}$, the negative sign being given to make this the expression of Lenz's law. The two equations

$$\epsilon = -\frac{dF}{dt} \text{ and } F = S.C$$

give, when S is constant,

$$\epsilon = -\frac{d(SC)}{dt} = -\frac{S dC}{dt}$$

Hence, when $\frac{dC}{dt}$ is positive, that is, the current is increasing, there is a negative E.M.F. due to self-induction, when $\frac{dC}{dt}$ is negative, that is, the current decreasing, the E.M.F. of self-induction is positive. Whenever the current is of constant value

$$\frac{dC}{dt} = 0$$

the E.M.F. of self-induction is zero. These expressions are adequate to interpret the phenomenon of photo-chemical induction, and further, in an approximate manner, the phenomena of fluorescence and phosphorescence, which correspond to the case when the "extra-current" of self-induction takes visible form.

§ 101. Energy necessary to establish a Steady Change; the Intrinsic Value and Inertia of a System.

If, electrically speaking, there were no such thing as self-induction, an E.M.F. E applied to a circuit of resistance R, would instantly occasion a current of strength $C = \frac{E}{R}$. Similarly, if there were no such thing as residual affinity, chemically speaking, or idio-chemical interaction,[1] every mechanical modification of a system, every impulse, applied to a system in equilibrium, would instantly give rise to a proportionate physical displacement. A perfectly mobile fluid would correspond to such a state of affairs. But the E.M.F. of self-induction entails a more or less gradual process in establishing a current, and the same is true of a chemical change, of which indeed an electric current is a single valued manifestation.

[1] Comprising the resultant of both idio-chemical attraction and idio-chemical repulsion.

During the variable period at the commencement of a current (or displacement of a quasi-static equilibrium) more energy is afforded to the receiving system from the source than it disposes of or transmits. This energy is stored up in the receiving system and increases its total energy. In a circuit with no variation of the flux, no self-induction, we have for the energy-consumption per unit time

$$EC_0dt = C_0^2Rdt$$

C_0 being the current in this state of invariance. Taking variation and self-induction into account, we have

$$ECdt = C^2Rdt + CdF$$

where C, the current, is not the same as C_0. dF is an increment of the flux of force through the system due to a variation in an independent field of force. Representing the total flux as before by $F = SC$, we have $dF = SdC$, and hence we can transform the foregoing equation to

$$ECdt - C^2Kdt = ZCdC$$

when $ZCdC$ is the excess energy stored up and not instantly transmitted.

If we write W for the total energy thus stored up while the current changes from a definite initial value C_0 to a definite final value C_1 we have

$$W = \int_{C_0}^{C_1} SCdC = \tfrac{1}{2}S(C_1^2 - C_0^2)$$

If the initial value of C_0 be zero, this gives

$$W = \tfrac{1}{2}SC^2$$

as the work necessary to establish the circuit. Suppose E be the total E.M.F. of the source, R the total resistance, S the self-induction of the system, and C_1 the final strength of the current when uniform, *i.e.* $C_1 = \frac{E}{R}$.

All the time the current is increasing in strength from o to C_1, we have for the E.M.F. at any instant

$$E = CR + S\frac{dC}{dt}$$

which we can write

$$\frac{E}{R} - C = \frac{S}{R} \cdot \frac{dC}{dt}$$

$$= -\frac{S}{R} \cdot \frac{d\left(\frac{E}{R} - C\right)}{dt}$$

since E and R are constant.

Rearranging, we get

$$\frac{d\left(\frac{E}{R} - C\right)}{\frac{E}{R} - C} = -\frac{R}{S}dt$$

or, calling the expression in brackets U

$$\frac{dU}{U} = -\frac{R}{S}dt$$

$$i.e. \quad \frac{d \log_e U}{dU} = -\frac{R}{S}dt$$

Integrating, for a time-interval such that $\frac{C_2}{C_1} = 1$ at the time $t_1 = t$, o when $t = o$, we get

$$\log_e U - \log_e (U + C) = -\frac{R}{S}t$$

and, rearranging and setting up inversely

$$C = \frac{E}{R}\left(1 - e^{-\frac{R}{S}t}\right) = C_1\left(1 - e^{-\frac{t}{\lambda}}\right)$$

where E is the base of natural logs, and λ is the quotient of the self-induction of a varying circuit. It is usually called its time-constant. Once the variable period of establishment of a circuit of induction of a definite chemical reaction is accomplished, its time-constant is negligible.

§ 102. The Deduction Period.

If, when the current has become steady, the impressed E.M.F. is cut off (as when in a photo-chemical change the light flux is interrupted) the resistance may be regarded as unchanged, but the value of E becomes o. Hence we have

$$CR + S\frac{dC}{dt} = o$$

whence

$$\frac{dC}{C} = -\frac{R}{S}dt$$

Then, for integration, we have, when $t = o$, $C = C_0 = \frac{E}{R}$

and

$$\log_e \frac{C}{C_0} = -\frac{R}{S}t = -\frac{t}{\lambda}$$

$$i.e.\ C = C_0 e^{-\frac{t}{\lambda}}$$

a law which characterizes also the falling away of the photolytically induced chemical activity of a chemical element.

These laws hold for the simple case of a single electrical impulse, which would correspond to a momentary exposure of a system to light. When a series of such impulses are afforded in more or less rapid succession, it frequently happens that not only the electric-motive force has to be considered as variable, but also the resistance. There are phenomena of photo-electric and photo-chemical fatigue and recovery which correspond to this which will be referred to later.

§ 103. Induction with Chlorine and the Draper Effect.

Draper[1] considered that chlorine which was insolated, *i.e.* exposed to radiant energy, was rendered active, that is to say, that its chemical affinity was enhanced. He found that chlorine previously exposed to light combined more

[1] J. W. Draper, *Phil. Mag.*, [3] **25**, 1 (1844).

readily with hydrogen in darkness or weak light than non-insolated chlorine. This statement was traversed by Bunsen and Roscoe, by Becquerel and others, but Bevan[1] has shown that failure to reproduce this Draper effect was due to passing the chlorine subsequent to insolation through water, which deprived it of its induced activity. Actually, this activation has been confirmed by several observers, and it is found that it may be produced not only by sunlight and artificial illuminants, but also by the silent discharge, and that, with suitable precautions, it can be brought about almost instantaneously. The deduction of the activity, with respect to hydrogen, was found by Mellor[2] to fall off according to the exponential function

$$a = a_0 e^{-kt}$$

the value of the "damping coefficient," the reciprocal of λ, the time-constant considered in the foregoing discussion, being 2·2. Russ[3] found that chlorine exposed both to light and the silent discharge (*effluve electrique*) acquired an activity with regard to benzene, the influences superposing, but varying with the dryness and temperature of the gas. Both moisture and heat accelerated the deduction.

From a study of the reaction in light between chlorine and carbon monoxide, Wilderman[4] concluded that the phenomenon of induction required the assumption of a new "light kinetic potential *sui generis*" by the absorbing substance. E. Baur[5] terms this capacity of the insolated molecule its "light-content," on the analogy of capacity for heat, and postulates that the period of induction is that required for the installation of this state. The reaction-heats of substances interacting in light must differ from those of the same reactions in the dark, the entropy being differently affected. As we have seen, self-induction in electric currents is a quantity of the same kind as mutual induction. If two circuits, each traversed by a current, are in

[1] *Proc. Roy. Soc.*, **72**, 5.
[2] *Proc. Chem. Soc.*, **20**, 140.
[3] *Chem. Centr.*, **1**, 1489 (1905).
[4] *Zeit. phys. Chem.*, **42**, 89 (1903).
[5] *Zeit. phys. Chem.*, **63**, 683 (1908).

presence of each other, the total energy is not simply the arithmetical sum of the intrinsic energies of the separate circuits, but equals this plus the energy due to their co-existence. If C and C′ are the strengths of two currents, S and S′ the two coefficients of self-induction, and M the coefficient of mutual induction, the total energy is

$$T = \tfrac{1}{2}SC^2 + \tfrac{1}{2}S'C'^2 + MCC'$$

We should expect, therefore, that where molecules of different kinds are insolated together, preferential activity would be shown between species for which *M*, the coefficient of mutual induction, had the largest value. This view is in harmony with the part assigned to the formation of intermediate compounds in chemical change. In the case of photo-chemical reactions, it is rare that examples of one single or even of two species of bodies are insolated, both the matter and the radiant energy are generally more heterogeneous, so that the resultant change depends upon the settlement of many minor encounters before it can be characterized as uniform.

§ 104. Intermediate Compounds and Pringsheim's Theory.

For this reason, much is often to be learnt concerning the nature of a change by making the insolation definitely intermittent. Pringsheim[1] submitted the hydrogen-chlorine mixture to light from an intermittent discharge. He found that there was a rapid preliminary expansion (that is, a counter-effect to the contraction indicating combination) followed by a rapid return to zero and then a slower contraction. Budde[2] observed the same effect with chlorine alone, and suggested that a dislocation of the chlorine molecule into atoms took place:

$$Cl_2 \rightleftharpoons Cl + Cl$$

Pringsheim partially adopted this view, and considered that then the chlorine atoms reacted with water-vapour to form

[1] E. Pringsheim, *Ann. Phys. u. Chem.*, **27**, 384 (1874).

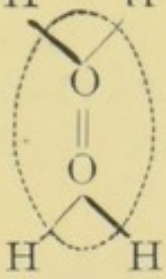
[2] *Pogg. Ann.*, **144**, 218 (1871).

chlorine monoxide. Here it may be pointed out that supposing the dissociation to take place and consequently into electrically equivalent doublets, so that this expanded phase of the chlorine might be represented by some such configuration as that on the right hand of the scheme :—

$$2Cl_2 \underset{\text{u.v. and dark heat}}{\overset{\text{light}}{\rightleftharpoons}} \begin{matrix} \overset{+}{Cl} & \overset{-}{Cl} \\ \vdots & \vdots \\ \underset{-}{Cl} & \underset{+}{Cl} \end{matrix}$$

then the radiation absorbed as light by the chlorine molecule may be regarded as anomalously dispersed, and as re-emitted as infra-red and ultra-violet rays on re-contraction of the expanded phase, above all in the presence of matter capable of having its equilibrium perturbed by such radiations, but not by ordinary light: for example, the chain of perturbations of the equilibrium of oxygen and hydrogen, originally in the form of double molecules of H_2O, may be represented as regards the *thermal* effect, by

$$H_4O_2 \rightleftharpoons 2(H.O.H) \rightleftharpoons H \quad H \rightleftharpoons 2H_2 + O_2$$



for the thermal *molecular* dislocation; and as regards the necessarily concomitant idio-chemical change in the independent elements

$$2H_2 \rightleftharpoons \begin{matrix} \overset{+}{H} & \overset{-}{H} \\ \vdots & \vdots \\ \underset{-}{H} & \underset{+}{H} \end{matrix} \qquad 2O_2 \rightleftharpoons \begin{matrix} \overset{+}{O} & \overset{-}{O} \\ \vdots & \vdots \\ \underset{-}{O} & \underset{+}{O} \end{matrix}$$

for ultra-violet atomic dislocation.

The essential feature is the generation of the *nascent* state of the elements concerned, with the consequent opening up of greater chance of formation of otherwise difficultly attainable combinations, formed on cessation of the light-ray as new

equilibria, in which the constituents are grouped or ordered in a different manner.

Pringsheim drew attention to the importance of the vapour-pressure of water for the reaction between chlorine and hydrogen. He found, using instead of water alone as the indicating liquid, water saturated to its full capacity with hydrochloric acid, that the action on exposure to light was diminished to $\frac{1}{50}$ of its value. (This agrees with the reversibility of the reaction

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

in ultra-violet light as found by Coehn.) He suggested that the reaction occurred in two stages, involving the decomposition and recomposition of a water gas-molecule as follows :—

I. $Cl_2 + H_2O = Cl_2O + H_2$
II. $4H_2 + Cl_2O = H_2O + 2HCl$

Mellor has objected against this that Cl_2O is more soluble in water than hydrochloric acid, in the proportion of 5 : 1. But this does not necessarily militate against the intermediate formation of Cl_2O in a skin of hydrogen, a shell temporarily protecting it against dissolution in water.

Gautier and Helier[1] suggested as an alternative sub-cycle, the two reactions

I. $Cl_2 + H_2O = HOCl + HCl$
II. $H_2 + HOCl = H_2O + HCl$

Against both these Mellor finds that the addition of traces of Cl_2O and HOCl to the reacting mixture has little effect on its course. He suggests that an indefinite adsorption-complex of $H_2O/Cl_2/H_2$ is formed, which then splits up, yielding HCl and water.

The probability of the formation of some kind of intermediary complex is strengthened by two sets of facts. The first is the phenomenon noticed by Pringsheim, that under certain conditions the reaction in light was attended with an audibly evident pulsation (knitterndes Geraüsch), which would be consequent with an oscillating discharge of electro-static

fields giving rise to acoustic waves of small amplitude. Photophonic phenomena of this type have been observed in other cases, with porous solid media, and are obviously contingent to a photo-chemical change in a gaseous medium of some mass, propagated through it in small explosion-waves.

The second is the nucleation and formation of clouds already referred to under the general discussion of the action of ultra-violet rays. As remarked then, this phenomenon is intimately dependent upon the presence of traces of vapours, analytic impurities in regard to the primary reaction, and which can act sometimes as positive but more often as negative catalysts to the reaction selected as of principal interest. So far as concerns the *chemical* explanation of the variable initial period (analyzed by Pringsheim, in the case of H_2, Cl_2, water-vapour, into (*a*) preliminary recoil, with no formation of HCl, (*b*) sub-period of *acceleration* of rate of formation, (*c*) steady period with uniform rate of formation), we have the following four kinds of explanation :—

(i.) Idio-chemical induction of the atoms of the elements, or period of attainment of their light-content (Draper, Wildermann, Baur).

(ii.) Formation of definite, singular intermediate compounds, breaking up to molecules different from the original ones to some extent (Pringsheim, Gautier, and Villers).

(iii.) Formation of indefinite adsorption or addition complexes, yielding hydrochloric acid as by a process of isothermal distillation. Compare the suggestion of Mellor. This hypothesis agrees roughly with Weigert's postulation of heterogeneous nuclei, similar to or identical with the nuclei of condensation in vapours (p. 303).

(iv.) Negative catalysis, due to traces of "impurities," which enter into side-reactions with one of the components. This explanation regards the retardation as the time taken in destroying or removing impurities, rather than as that essential to the formation, duration, and decomposition of intermediate bodies.

Such may be formed in small quantities, but they are not necessarily indeterminate, but rather minute quantities transiently formed of well-known bodies (Chapman and Burgess).

These explanations all compenetrate or overlap to some extent, and, chemically, it is possible that the variable period is determined rather by an indefinite number of contributory causes than due to a single origin.

So far as Pringsheim's theory is concerned, it appears certain that water-vapour plays a considerable part in this as in many other reactions.

§ 105. Condensation-Nuclei.

The influence of ultra-violet light in precipitating saturated vapours in the form of fog or mist, aggregates of microscopic and ultra-microscopic droplets which, if not again dissipated, condense and fall as a fine rain, has already been mentioned. It will be remembered that *true gases* and *vapours* are states of matter which merge quasi-imperceptibly into each other according to the "saturation" of the vapour.[1] There is evidence that this "saturation" of the vapour phase is concomitant with the degree of association of the single gas-molecules in molecular-complexes of different orders of association, but this image from the molecular kinetic theory is drawn in to supplement the inadequacy of thermodynamics when transferred from the general statement of abstract relations between ideal systems to the specific facts of practical experience.

By definition, a vapour is "saturated" when in equilibrium with a definite mass of the liquid phase. As is well known, it is possible to find a particular congruence of temperature, pressure, and body of many substances for which the usual evidence of mechanical discontinuity of state between vapour and liquid disappears. This point is known as the critical point, only it should be noticed that its arrival is simultaneous

[1] Cf. S. Young, *Stoichiometry*, this series, p. 114.

with the appearance of a fine optical heterogeneity or opalescence in the system.[1] There is evidently a partial segregation of the substance, even here, into loci of alternate condensation and rarefaction, of greater and lesser density. These inhomogeneous portions cannot be termed actually liquid and gaseous, for the overt characteristics of these states are temporarily suspended at the critical point, but they are potentially so. We may term them, to fix our ideas, liquido-genic and gaso-genic respectively, and remark that a definite interfacial tension must obtain between the molecules in the one and the other disposition.[2]

That a real difference exists between the liquido-genic particles and the gaso-genic ones is strongly suggested by the essential facts characterizing the critical point. It does not suffice to compress a gas to liquefy it, if one does not simultaneously diminish its internal heat, lower its temperature. This one effects most readily, ultimately, by first submitting the gas to considerable compression, then allowing it opportunity to suddenly expand in one direction.

Synchronously with the pulse of rarefaction but opposite in sense, that is, back into the deeper layers of compressed gas, there travels a pulse of condensation, the course of which is traced by the formation of liquido-genic particles, owing their genesis to the Joule-Thomson effect in the gas. These particles are readily grouped to a true fog-nucleus or colony of such nuclei, and, with sufficient precautions as to auxiliary cooling and shielding from radiation, on repetition of the process, sensible quantities of liquid are obtained.

What is characteristic, for a critical temperature fixed by the nature of the body, of the kind of condensation effected (whether stationary mist or falling rain, or what not) is the ratio of $\frac{\text{compression pressure}}{\text{expansion pressure}}$ in a stroke. *Ceterus paribus*, for the same substance, the greater this ratio the more definite the *permanent alteration* of state effected. Thus, it must be

[1] Cf. S. Young, *Stoichiometry*, this series, pp. 122 *et seq.*

[2] Cf. G. Bakker, "Théorie de la Couche Capillaire Plane des Corps Purs.," *Scientia*, No. 32 (Gauthier-Villars, Paris, 1911).

greater to effect opaque cloud-formation than for translucent mist. *Per contra*, preliminary addition of nuclei, such as dust, will lower the value necessary to effect the same apparent alteration.

We are dealing here with a phase of the general problem of the propagation of waves of shock in a continuous medium. The ratio in question is closely analogous to Hugoniot's "coefficient d'élasticité adiabatique isothermal" a.[1] Now, one way of introducing nuclei in the system which *depress* the coefficient a, *i.e.* the value of this for a specific stage of development of the liquid state, is the insolation of the gas-vapour medium by radiant energy. The following tables show the results of experiments in this way with (water-vapour, chlorine) and (water-vapour, chlorine, and hydrogen) :—

TABLE XX.

From Bevan, *Phil. Trans.*, A. 202, 71 (1904).

System.	Appearance.	$a = \frac{p_1}{p_2}$ in light.	a in dark.
Chlorine (water-vapour)	Fine rain	1·30	—
	Cloud	1·46	1·50
Chlorine	Rain	1·22	1·42
Hydrogen (water-vapour)	Cloud	1·32	—

Not only is a definite influence of light shown, but it would seem to be more marked when the reaction forming hydrochloric acid was possible. Further, when the formation of the acid had started, it was found that "expansion" to the cloud stage stopped the formation.

[1] H. Hugoniot, *Journ. Maths. pures. app.*, [4] **3**, 477 (1887) ; **4**, 153 (1888). Cf. also J. W. Mellor, *Statics and Dynamics*, this series, p. 460.

TABLE XXI.

From Burgess and Chapman (*loc. cit.*).

System.	Appearance.	a intense white light.	a feeble white light.	a yellow light.
Cl_2 (water-vapour)	Fine rain	1·30 to 1·35	1·43	1·42
	Rain	1·33 to 1·38	1·44	1·45
	Cloud	1·38 to 1·42	1·47	1·47
	Fog	1·46	1·51	1·51

From their experiments Burgess and Chapman conclude that the formation of these nuclei is not essential to the production of hydrochloric acid. But there seems considerable evidence in favour of the view that the physical condensation (change of aggregation-state of water, etc.) and the chemical metathesis are absolutely concomitant and interdependent. The process of diffusion, for example, is too often treated as if it were a single-valued mechanical process, uninfluenced by chemically selective considerations, a view which the specific chemo-taxes and tropisms of colloid particles entirely contradicts. What is peculiar to the nuclei in the chlorine-hydrogen photolysis is that electrically they seem stubbornly neutral. J. J. Thomson could detect no free ions in an insolated mixture of chlorine-hydrogen, neither during nor after the Draper effect, and this is confirmed by Lenard.[1] But, save when a unilateral field of force is employed to measure the charge, velocity, and magnitude of these corpuscular rays, it is possible that they travel rather as Bragg suggests for Röntgen-rays, as neutral couples or neutrons of α and β rays, and that this neutral couple, when impeded in the gas-mixture, effects the metathesis without there being necessarily any evection of free-charged particles, which, as Lenard points out, is not necessarily a feature of free photo-chemical change, but more often a forced side-issue, very possibly antagonistic in its working to the progress of photo-chemical change proper.

[1] *Sitz. ber. Heidelberg. Acad.*, Abh. 31, 1 (1910).

§ 106. Induction and Negative Catalysis.

The influence of traces of analytic impurities on the combination of chlorine and hydrogen was noticed by Bunsen and Roscoe, as well as the sensibility of the variable period of induction to these.[1] They found that small quantities of air could greatly dilate the variable period, and appreciably depress the maximum (uniform) velocity. Excess of hydrogen beyond the theoretical equivalent proportion depressed this also, and prolonged the induction. Thus 0·3 per cent. excess lowered it from 100 to 37 per cent., 0·5 per cent. of oxygen from 100 to 4·7 per cent., 1·3 per cent. of oxygen from 100 to 2·7 per cent., excess of chlorine having much less effect. As it is convenient to have a single name for these effects of gases on each other's reactivity, we shall occasionally use the term "atmolysis" to cover the ambit of the phenomena. Wilderman, in his investigation of the formation of phosgene in light, observed similar interference of added gases and impurities; whilst G. Dyson and A. Harden[2] observed that the induction-period for this reaction was very variable and dependent on the preliminary stages of preparation.

Burgess and Chapman, having arrived at the conclusion that the variable period of induction was, chemically considered,[3] predominantly engendered by the presence of foreign substances in small quantities, made a very careful search on the nature of the inhibitive substances in the $H_2 \sim Cl_2$ reaction. They obtained the following results:—

(*a*) Ammonia, or compounds capable of yielding ammonia, in the mixture of chlorine and hydrogen gives rise to marked photo-chemical induction.

(*b*) Impure water contains compounds only slowly destroyed by chlorine at ordinary temperatures.

(*c*) The impurities yielding ammonia may be removed by chlorine in light, or by heating to 100° C.

[1] *Pogg. Ann.*, **100**, 500 (1855).

[2] *Trans. Chem. Soc.*, **83**, 201 (1903).

[3] The specific chemical interpretation of the origin of induction does not affect the mathematical theory.

(*d*) The actual inhibitor in the case of ammonia is probably NCl_3, as direct addition of this compound produced the symptoms. If freed from impurities, slight excess of either hydrogen or chlorine does not affect the sensitiveness.

The inhibitory action of NCl_3 is attributed by Chapman and Burgess to the installation of the sub-cycles

$$NCl_3 + 3HCl \rightleftharpoons NH_3 + 3Cl_2$$
$$NCl_3 + 3H_2O \rightleftharpoons NH_3 + 3HClO$$

by which a certain equilibrium-concentration of ammonia would be maintained, and the actual formation of HCl reduced.

Other experiments showed that SO_2 could act as an inhibitor, and, in agreement with Bunsen and Roscoe's work, and with Goldberg's research on the photo-chlorination of benzene, that free oxygen can play a great *rôle* in such atmolyses. As in the case of ammonia, the oxygen is used up or fixed in the interaction but may be re-supplied from the walls of the vessels, thus originating a fresh inhibition. Burgess and Chapman suggest that in this specific case (formation of HCl) its effect may be represented by the scheme

$$O_2 + 4HCl \rightleftharpoons 2Cl_2 + 2H_2O$$

Everything points in these photo-chlorinations to chlorine itself as being the preponderantly light-sensitive substance, the reactions with hydrogen, ammonia, sulphur dioxide, organic vapours, instantly developing, as it were, the latent image impressed by light on the chlorine. In consequence, the activated chlorine can, as we shall see, act as a photo-ferment to other reactions not directly sensitive to light.

§ 107. The Rôle of Oxygen in Photo-chemical Changes

The marked desensitizing effect of oxygen in photo-chemical change was observed by E. Goldberg[1] for the

[1] *Zeit. phys. Chem.*, **56**, 43 (1906).

photo-chlorination of benzene, the efficiency of which can be enormously raised by scrupulous elimination of oxygen, or conversely, greatly impeded by its introduction. The same holds for the photo-chlorination of xylol, etc. Goldberg suggests that oxygen may be regarded as a specific poison to chlorine in regard to photolysis, but the same action of oxygen has been shown by Iodlbauer and Tappeiner[1] and by C. Winther[2] to interfere similarly with the sensibility of the mercury oxalate ~ oxalic acid actinometer of Eder, and there is evidence that it plays some part in the photolysis of the silver halides (*vide* p. 371).

Recent experiments of Chapman and Burgess have shown that on carefully removing oxygen from an electrolytically prepared mixture of chlorine and hydrogen, the sensitiveness of the mixture to light, as measured by the rate of combination, may be indefinitely increased by the purification, tending to become infinite as it is pushed to extremes. This may be expressed as follows. Suppose the effective energy stored up on absorption by chlorine from mono-chromatic light of intensity J be (ΔE) per unit volume, and let $[O_2]$ be the amount of oxygen present in this volume. Then as a first approximation we may write for the rate of discharge of this energy

$$-\frac{d(\Delta E)}{dt} = K_2(\Delta E)[O_2]$$

Since oxygen is very transparent for the part of the visible (and neighbouring invisible) spectrum absorbed by chlorine, we can write the rate of charging of the chlorine by light as

$$+\frac{d(\Delta E)}{dt} = K_1 J$$

where J is the light-intensity.

Hence, in the steady state when the processes are equilibrated we shall have for the photo-chemical equilibrium

$$K_1 J = K_2(\Delta E)[O_2]$$

or

$$(\Delta E) = \frac{K_1}{K_2} \cdot \frac{J}{[O_2]}$$

[1] *Ber.*, **38**, 2602 (1905). [2] *Zeit. wiss. Phot.*, **7**, 409 (1909).

the ratio $\frac{K_1}{K_2}$ being the economic coefficient. Hence, the effective energy at any instant in the steady state is directly proportional to the light intensity and inversely to the concentration of oxygen. We may assume that the velocity of combination of chlorine with hydrogen is proportional to this effective energy, the reaction

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

being made unilateral and complete by exclusion of reversing factors.

In consonance with this hypothesis they found that the product of sensitiveness multiplied by the concentration of oxygen was approximately constant, indicating an inverse relation between the initial velocity of change and the concentration of oxygen. These experiments indicate that the inhibition afforded by oxygen is rather of the nature of an active impedance, consequent upon the exercise of its affinity, whether with chlorine or hydrogen, or both.

It has been shown by C. Winther[1] that oxygen plays a similar *rôle* in the photo-catalysis of the reaction of a solution of mercury bichloride and ammonium oxalate in light. Upon insolation, this double solution deposits mercurous chloride and gives off carbon dioxide. It is usually termed Eder's solution, having been adapted by this photo-chemist to actinometric usage.[2] Eder noticed that there was an induction-period, the reaction being followed by weighing the calomel precipitated, and this he attributed to the necessity of the solution becoming saturated (or rather, supersaturated) with the sub-salt before precipitation could occur. Further he showed that there was a considerable optical extinction concomitant with the reaction, for the effective region of the spectrum. In a subsequent investigation of the change, Roloff[3] came to the conclusion that the actual reaction did not take place either between the undissociated

[1] On the Eder solution, *Zeit. wiss. Phot.*, VII., 409 (1909).

[2] J. M. Eder, *Sitz. ber. d. Wien. Akad.*, 1879.

[3] *Zeit. physik. Chem.*, **13**, 329 (1894).

molecules, nor between the complexes which the solution could be shown to contain, but between free mercury ions and oxalate ions, according to the scheme

$$2Hg^{\cdot\cdot} + C_2O_4'' = 2Hg^{\cdot} + 2CO_2$$

This he supported by the effect of different additions—chloride, nitrate, and mercury ions, and carbon dioxide. The last had the unexpected effect of increasing the sensitiveness, which Roloff attributed to "optical" sensitizing (*vide* later, p. 435). It would be quite possible, however, that it acted auto-catalytically in helping to discharge the carbon dioxide yielded by the reaction. Later researches of Iodlbauer and Tappeiner[1] showed that passing a current of hydrogen through the reacting solution had the same effect, as well as evacuation, whilst purified oxygen (up to 2 atmospheres, pressure) showed a powerful desensitizing action. Already Kastle and Beatty[2] had found a series of positive catalysts, acting in very small concentrations, as well as certain negative catalysts, for this reaction. Later, Gros,[3] working on the light-sensitiveness of fluorescein dye-stuffs, found that small quantities sensitized the Eder solution. This was further investigated by Iodlbauer and Tappeiner,[4] who tried a great number of fluorescent dye-stuffs, and found that only the fluorescent ones were effective.

Winther's investigation was concerned with a prolongation of Kastle and Beatty's work. The positive catalysts found by these workers were—potassium permanganate, iron chloride, iron alum, gold chloride, platinic chloride, thallium chloride, chrome alum, uranium nitrate, potassium bromate, ammonium persulphate, chlorine water. As negative catalysts, potassium chromate, bichromate, and chromic acid.

Considerable difference in the strength of the catalytic influence of these was observed. Winther found that cerium salts, potassium ferricyanide, and potassium iodide (in defect),

[1] *Ber.*, **38**, 2602 (1905).
[2] *Amer. Chem. Journ.*, **24**, 182 (1900).
[3] *Zeitschr. phys. Chem.*, **37**, 157 (1901).
[4] *Loc. cit. Ber.*, **38**, 2602 (1905).

retarded the change, in decreasing order of efficiency, whilst potassium iodide (in excess), copper salts, potassium tin chloride, and many organic dye-stuffs accelerated it.

It is noteworthy that practically all these bodies contain in the higher stage of oxidation elements capable of more than one oxidation stage. Yet such oxidizing agents appear both as positive and negative catalysts. Winther succeeded in showing that the chlorine water was not a true photo-sensitizer since it had the same effect in darkness upon the precipitation of calomel. Its influence is due to the coupling of the rapid reaction between chlorine water and ammonium oxalate with the slow reaction between ammonium oxalate and mercuric chloride, the chlorine-water being decomposed in definite and small proportionality to the calomel precipitated.

Further experiments showed that the kations Fe, Mn, Ce were peculiarly effective photo-catalysts for the reaction. In the case of iron salts, the essence of the process was found to consist in—

(i.) Rapid reduction by light of ferric oxalate.

(ii.) The ferrous iron thus formed reduces mercury chloride, precipitating calomel.

(iii.) Since the ferrous iron produced in the first reaction is susceptible to autoxidation by dissolved oxygen, reduction of the concentration of this last accelerates the precipitation of calomel.

(iv.) Excess of ferric salts prevent the precipitation of calomel, hence there is an optimum concentration of the ferric iron for photo-catalysis. This inhibition increases considerably, for a given concentration of ferric salt, with the diminution of the oxygen concentration, so that the optimum concentration of iron varies with the concentration of oxygen present.

In a further communication on the subject, Winther states—

(i.) The induction-period is the time during which the dissolved oxygen is mostly consumed.

[1] Winther concludes that it has nothing to do with the "time of saturation" of solution with calomel. But, as in the case of gas-reactions

(ii.) The inhibiting action of oxygen increases rapidly as the concentration of iron is diminished.

(iii.) With increasing concentration of iron, the position of maximum spectral sensitiveness is displaced from the ultra-violet to the visible spectrum, so that the spectral sensitiveness curve depends upon the content of iron.

(iv.) No evidence for an essential photo-chemical extinction of light (*vide* p. 187) could be obtained with this reaction.

(v.) The light-sensitiveness of Eder's solution is due to the presence of *iron*, and is directly proportional, other things being equal, to the concentration of this.

(vi.) The purest Eder solutions so far prepared have contained iron. In the absence of this, mercury oxalate is not sensitive to visible rays. Up to $\lambda = 313\ \mu\mu$ the Eder solution does not absorb more strongly than plain water; beyond that it has its own ultra-violet absorption.

This investigation is of singular importance in exhibiting such a well-known substance as iron as a definite photo-sensitizer. At the same time, just as it confirms the view that the distinction, for photo-chemical reactions, between "optical" and "chemical" extinction of light is a very artificial one, incapable of experimental decision, so also the distinction between optical and chemical sensitizers for photo-chemical reactions is equally artificial, there being no real difference between them. Before, however, dealing with sensitizing by dye-stuffs in relation to the practically important silver salts and in organic photo-synthesis, we will deal with Weigert's researches on "photo-ferments."

in light, the production of a precipitate in a coherent, coagulated form is not entirely independent of the chemical changes occurring in the system, but is rather intimately dependent upon them. Thus the iso-electric point necessary for the precipitation of colloid-complexes is a function of the reaction between the simpler electrolytes in a solution. It is interesting to note that Iodlbauer and Tappeiner observed a distinct difference in the texture of the calomel precipitate when the oxygen was withdrawn. Instead of a definitely micro-crystalline deposit, there was a flocculent, cloudy, colloid suspension.

§ 108. Formation of Phosgene and Photo-ferments.

The photo-synthesis of phosgene ($COCl_2$) from chlorine and carbon-monoxide discovered by Davy, has been studied by several observers. G. Dyson and A. Harden[1] noticed a decided "variable period" of induction, and the influence of air, water-vapour, carbonyl chloride, and hydrochloric acid on the reaction. M. Wilderman[2] made a very careful examination of this reaction, in which exceptional precautions were observed in the control of the constancy of the light-sources and in the purification of the material. The progress of the reaction, carried out in a thermostat, was measured with a manometer, which showed the difference in volume of the uncombined and combined gases. Theoretically

$$\underset{2\text{ vols.}}{CO + Cl_2} = \underset{1\text{ vol.}}{COCl_2}$$

Once the induction-period was passed, which Wilderman attributed to the excitation of the absorbing molecules to a new light-kinetic potential, he found that the reaction followed, for constant light-intensity, the ordinary mass-law, the course being given by the usual bimolecular formula

$$\frac{dx}{dt} = K(a - x)(b - x)$$

where x is the amount of substance converted, a and b the original concentrations or active masses of the reacting bodies. The velocity-constant K is proportional to the intensity of light. This formulation has been regarded as flatly contradictory to any possibility of photolysis following a law similar to the law of electrolysis of solutions discovered by Faraday, according to which the rate of decomposition is proportional to the energy-consumption per unit interval of time and independent of the masses of the reacting substance. The whole logomachy on this point seems to result from a misunderstanding, and a confusion of *relative*, *differential* rate of transformation, which can only be inferentially determined

[1] Eder's *Jahrb. f. Phot.*, 1903, p. 408.
[2] *Zeitschr. physik. Chem.*, **41**, 87 (1902).

to an arbitrary additive constant, and absolute *integral* rate of transformation, as actually measured in finite differences experimentally, when a suitable value has to be assigned to the additive constant. In electrolysis, the assumption that the rate of electro-chemical decomposition is proportional to the energy consumed per unit time necessarily presupposes that it is identically proportional to the active mass of the substrate, which, however, in so far as the transvection across a plane section of the system of reacting material is maintained constant (uniform period when Ohm's law is strictly followed) is resupplied by the synchronous electro-osmosis at the same rate that it is electrolytically decomposed, so that, theoretically, for the simplest limiting case, the rate is independent of the active mass. In order that Wilderman's results should show a categorical contradiction between the processes of photolysis and electrolysis, it would be necessary to conduct experiments, not only at constant temperature and light-intensity for one value of the actual initial concentrations a and b (which are usually, in view of the stoichiometric relation of *static equilibrium* already determined, made equivalent, hence simplifying the kinetic equation which becomes

$$\frac{dx}{dt} = \mathrm{K}(a - x)^2$$

but also with a wide range of initial values, *i.e.* of working pressures in the actinometer, which is, from its construction, also a manometer. If the comparison between electrolysis and photolysis is justified, one should find a superior limit to the velocity for very high initial concentration, such as Luther and Weigert found for anthracene, when total absorption of light was effected. Also it must be taken into account that the foregoing bimolecular formula, which is found valid for the reaction course *disregarding the variable induction period*, would equally represent an autocatalytic "mono-molecular" reaction.

Wilderman postulates that a similar law holds for the mobile photo-chemical equilibrium as for thermo-chemical equilibrium, light effecting a displacement of equilibrium proportional to its "intensity." The application of this principle

to the case of phosgene is disputed by Weigert.[1] He finds that phosgene is decomposed at fairly high temperatures, according to the equation

$$COCl_2 \rightleftharpoons CO + Cl_2$$

there being at 500° C. 65 per cent. dissociation. Light simply accelerates the installation of this equilibrium from either side; that is, it acts purely catalytically. But the proposition that in such cases light does no work seems very questionable. As a mere matter of terminological exactitude it would seem that if light accelerates the decomposition of phosgene, in such a case it acts analytically, whilst if white light, or heterogeneous radiation were employed, one would, in consonance with the antagonistic activity of radiations of different frequency, anticipate the possibility of displacement and readjustment of the displacement of equilibrium, *i.e.* reversal as a function of the total duration of insolation, such as is observed with the silver halides. If we regard a system as completely characterized by its pressure P, temperature T, and a third variable S,[2] all states of the system for which a certain simultaneous relation between these three variables is not satisfied will be either unstable or meta-stable.

§ 109. Catalysis and Photo-chemical Change.

In order that idio-chemical change of constitution may take place in a single chemical element, which, like that typified in the scheme

$$2O_3 \underset{t'}{\overset{t}{\rightleftharpoons}} 3O_2$$

may be regarded as an allotropic or allophysical change of state in two parts of the same monovariant system, or that heterochemical change of kind of combination may take place with two chemical elements, as typified by the scheme

$$2HCl \underset{p'}{\overset{p}{\rightleftharpoons}} H_2 + Cl_2$$

[1] *Ann. Phys.*, (4) **24**, 25 (1907).

[2] Cf. P. Duhem, *Mécanique Chimique*, T. I., p. 209 (Paris, Hermann, 1898).

the presence of a third component frequently appears essential. But the two cases cited are not quite on all fours. There may be reason to postulate an extraneous determinant of the allotropic modification of state of a single element, for want of any overt reason of change, of, say, ozone molecules into diatomic oxygen-molecules, or conversely, but no such reasoning, *à priori*, seems applicable in the second case, because the postulated dissimilarity and heterogeneity of the two elements concerned is already nominally sufficient reason for at least an *intermittency* in their reciprocal relation, *i.e.* for a periodicity of some order in regard to the formations and dissolutions of their union. None the less, the facts grouped under the term "catalysis" exist, whether the explanation by a *tertium quid* be nearest the truth as to their origin, or whether the term be a cloak for our ignorances of the real nature of chemical change and of the idiosyncrasies of the elements in exercise of their elective affinities. What is most characteristic of nature is rhythm, alternation of matter and energy between relatively condensed and relatively dispersed states, between concentrated and diffused conditions. Continuous everywhere though this alternation be, it is often necessary locally to initiate or start change from one aspect to the other. There are equilibria in the diffused states as in the condensed states, which resist more or less stoutly any impulsion to change. To break down this inertia is the function of catalysts.

It is possible that the perfect medium (or catalyst equipotential both positively and negatively) between two allomorphic or heterogeneous elements is in no way really an absolutely extraneous factor, that so far as chemical union between two elements is concerned "the force of nature could no further go; to make a third she joined the other two."[1] On this view, which is in harmony both with the accumulating facts as to the specificity of catalysts when rigorously investigated, and with that regulative principle of scientific method which forbids the multiplication of hypotheses, of entities, and laws beyond necessity, a true catalyst is no extrinsic *tertium*

[1] That is, catalysis, to be effective, must involve auto-catalysis. Cf. E. J. Mills, *Phil. Mag.*, [5] **1**, 1 (1876).

quid, but a peculiarly indifferent and indissoluble conjunction of the two components of a reaction, which may be reduced in space, in quantity, to absolute minima, rendered latent in time for indefinite periods, but never permanently annihilated, indifferent to change because, in virtue of the intrinsic isodynamic disposition in antagonism of its elements, itself art and part of the pulse of change.[1]

In the benzene nucleus of organic chemistry we have in the centric skeleton already the suggestion of such a disposition of affinity, which is not destroyed by reactions breaking up "benzene," but merely passed on to other elements than those which entered in in the formation of "benzene." That is, the same configuration — and others analogous therewith, irrespective of the component elements subtending them, but which possess a measure of the isodynamic status—may be of like sovereign importance, though less permanently maintained in being, to other elements beside *carbon*. Thus it is feasible that a plane section of the common figure of interpenetration of two ozone molecules (ozone and ant-ozone) would give such a hexadic distribution of the force of affinity.

In the reaction—

$$2O_3 \rightleftharpoons 3O_2$$

it would be this *hexadic* equipotential configuration which would generate indifferently, on its self-division, two ozone molecules or three oxygen, in process of reducing its actuality, its mass of action, to a least value. And this expansion and contraction of the intermediate hexad we may regard as concomitant with the passage of a trace of another element very rapidly athwart the mass of oxygen, a passage engendering the centric configurations referred to. In the discussion

[1] That is, as E. J. Mills suggests, "We can understand how a chemical reaction is possible. It can begin because it has never ended—every substance retains a minute but real reserve of unexhausted energy." (*Phil. Mag.*).

of the structure and nature of flames and luminescent systems, this question will be returned to, as well as the part played by α-particles or anode rays in the radio- and photo-activation of reactions. In considering the sensible, physical stability of a mass of a substance such as benzene, its transitions *per se* from crystalline to liquid, liquid to gaseous states, there is of course no permanent nucleus necessary to the ring of a single molecule, but these rings may be conceived as strung along the curvilinear path of a rapidly moving α-particle, and the spatial arrangement of the benzene molecule undergoing stereo-isomeric transfigurations according to the phase of this labile centre.[1] The importance of such, so to say, minimally organized, but formative and organizing phases of matter is of the utmost importance in synthetic photo-chemistry, for it is apparently by means of such that vegetative life accomplishes the increasing adaptation of its organisms to their ambient medium and accomplishes the paradox of drawing down fire from heaven to form fuel of earth.

A physico-chemical system reacting to light usually (exception being made of certain markedly synthetic photo-chemical changes) stores up or retains but a small increment of the incident radiation (true conversion of light energy into intra-atomic chemical affinity), the major portion being merely redistributed whether as light, by transmission or reflection, or irradiated as heat through a series of level surfaces or zones about the centres of dispersion. The concomitant enhancement of movement of the physical molecules of the body is the increase of temperature, but, as will be more apparent on dealing with fluorescence, visible and invisible, that is, the transformation of radiations, we might if it were convenient, speak of this latter side-issue (irradiation) as infra-red fluorescence. It appears probable that for every illumination of a material system there is a displacement of equilibrium such that, for the new equilibrium in light, if we write for the mobile equilibrium in general the scheme—

$$\underset{\text{phase of concentrated energy}}{nX_m - \xi_t'} \rightleftharpoons \underset{\text{phase of dissipated energy}}{mX_n + \xi_t'}$$

[1] Cf. Ch. IX.

when n and m are numbers relative to the *total* and *specific* states of aggregation of the substance x, $|\xi|$ the quantity of energy between the limits t and t' of the *tension* of the transition, then the initial observable displacement is toward the phase denoted on the left-hand side of the equation as the phase of concentrated energy. That is, we may say, the system tends to pass into a state of photo-tonus. On stopping the excitation, this stimulus or photo-tonus exhausts or discharges itself more or less rapidly, which deduction period is, as indicated by the scheme, concomitant with an evolution of free energy. And following the recommendation of Hartley and Pollok[1] in regard to thermo-chemical notation, it will be convenient to generally refer to the phase of concentrated energy on the left-hand side of a transition as the *initial state*, the energy-sign ξ being here negative, and the correlative phase of dissipated energy, written on the right-hand side, the energy-sign being here positive, as the *final state*.

This usage is in consonance with the second law of thermodynamics, which asserts that a reaction, or a series of reactions, is realizable if it involve an increase of entropy, which may be expressed as follows: "The sum of all relative transformations in a realizable, non-reversible (or partially reversible) cycle, is necessarily positive."[2]

$$\sum \frac{d\xi}{t} > 0$$

A proposition which remains true for a cycle in part of reversible (ideal, virtual, or imperceptible oscillations) in part of realizable, non-reversible modifications. It is perhaps true that this consists in saying in somewhat legal phraseology that a change remains realized when it is not forthwith unrealized, *e.g.* that a knot remains tied if not undone or cut, but it is a proposition which has been of incalculable utility in the

[1] Cf. *Report of Seventh International Congress of Applied Chemistry*, Sect. X., Electro and Physical Chemistry. W. N. Hartley: "Proposal of a uniform system of thermo-chemical notation."

[2] Cf. P. Duhem, *Mécanique Chimique*, Tome I., p. 78 (Paris, A. Hermann, 1897).

establishment of rational thermodynamics, and must be considered rather as a critical turning-point in the evolution of the theory, than cut away and criticized in abstraction from the context. None the less, it seems extremely probable, as Duhem maintains,[1] that many thermodynamic and thermochemical equilibria are, in certain respects, properly designated as "false equilibria." The displacement of such by photoferments would not therefore be contrary to the generally accepted principle that a catalyst cannot permanently alter an equilibrium;[2] it would rather be an essential function of a catalyst to diminish the extent of a region of false equilibrium, such action being identical with its acceleration of the installation of a true equilibrium.

§ 110. Units of Energy and Transformation Equivalents of Light and Work.

In the specific case of physico-chemical change of oxygen represented by

$$2O_3 - \xi_t'' \rightleftharpoons 3O_2 + \xi_{t'}$$

the symbol $t|\xi|t'$, taken absolutely and independently of sign, simply refers to the definite quantity of energy proper to the transition of the substance between the limits of tension t and t', independently of the kind of work for which the energy might be utilized or made available to effect, hence without specification of the units it is to be measured in.

The partial tensions, t and t', are from a dynamic point of view, the velocity-potentials of the inverse reactions, and the dynamic balance obtains when these differ infinitesimally from each other, *i.e.* $t' = t \mp \delta t$.

Thermochemically, t and t' are measured as transition-temperatures, the transition being monotropic if t' differs only infinitesimally from t. At the same time, the energy

[1] P. Duhem, *loc. cit.*, "Faux équilibres et explosions," *Méc. Chim.*, Tome I. (2), p. 218.

[2] Cf. J. W. Mellor, *Chemical Statics and Dynamics*, this series, Ch. X., p. 250.

$|\xi|$ is measured in *calories*, major or minor, the specific reaction-heat being calculated per gramme-molecule of the substance in transition, due correction being made for associated changes of aggregation-state other than that proper to the reaction immediately in question. Now the mechanical equivalent of heat is determinate, but the mechanical equivalent of light is yet indeterminate, and, consequently, the thermal equivalent thereof (*vide* p. 78). But to be precise, it is necessary to point out that in the estimation of thermo-chemical equations, the energy evolved (or involved) is only accurately determined to a certain variable "radiation-correction." This. which it is an object in thermo-chemistry to reduce to a minimum, is from a photo-chemical standpoint precisely the important proportion of the energy-feature of a change. Only if accurate transformation-equivalents of calories (heat-energy units) with lumens (light-energy units) were known could the energetics and economics of photo-chemical change be satisfactorily elucidated. And this is correspondingly more difficult because of the highly differentiated character, involving multitudes of individual anomalies, of optical and photo-chemical change. Estimates so far from sundry specific reactions, whether of the light emitted by chemical change or of the amount of light converted into increase of affinity, point generally to only a small transformation-equivalent. Thus in the production of light, a large part of the energy is dissipated as heat in the absorption, a large proportion also goes to elevate the temperature of the mass.

§ 111. Photo-ferments and Catalysis.

Leaving the more theoretical aspect of the energetics of photo-chemical change for the moment, Weigert's conception of the nature of the kinetics and of "photo-ferments" demands attention. He considers that exposure of chlorine to light (insolation) effects some sort of heterogenesis in this, resulting in the production of nuclei which pervade the gas-phase, as colloid complexes of many molecules of different

types, and on or within the superficies of which the reaction takes place with greatly accelerated speed. So far this resembles in some degree Faraday's condensation-theory of contact-action.[1] Hence, these sub-microscopic nuclei (each a host of molecules in itself, on the principle that every crowd is a crowd of crowds, the unit of a true crowd being, as one may discern by experiment, a small crowd) behave similarly to the colloidal platinum and other such "inorganic ferments". which effect the decomposition of H_2O_2.[2] He considers that in the reaction of Cl_2 with CO_2 (or H_2) in light, what is usually measured is a diffusion-velocity of the components into the shells of the reaction-nuclei. Assuming that the gas-molecules diffuse in and out of the shell according to their diffusivities (which means a specific function of their mass, the concentration-gradient taken as unity, and of the viscosity of the medium) in the steady state the thickness of the shell may be reckoned constant. The heterogeneity is assumed to be sub- or ultra-microscopic, but considering the condensation experiments already detailed, may evidently be readily developed beyond the ultra-microscopic and microscopic limits.

In support of the view that the velocities observed are diffusion velocities, Weigert instances the temperature-coefficients of many photo-chemical changes, which are in general small and of the same order as those for velocities of diffusion (diffusivities).

TABLE XXII.

Reaction mixture.	Temperature-coefficient for 10°.	Observer.
Ferric oxalate to ferrous .	1·02	Lemoine.
Styrol → meta-styrol . .	1·34	Lemoine.
Oxalic and mercuric chloride (Eder's solution)	1·19	Eder.
Anthracene → dianthracene	1·21	Luther and Weigert.
Gelatino-silver bromide .	1·03	Lumière.
	1·00	Schellen.
Quinine and chromic acid .	1·04	Goldberg.

[1] Cf. J. W. Mellor, *Chemical Statics and Dynamics*, this series, p. 258.

[2] G. Bredig and K. Iheda, *Zeit. phys. Chem.*, **31**, 324 (1899).

This, however, is not absolutely cogent, since with many reactions the temperature-coefficient steadily decreases as the absolute temperature is increased, and in many respects photo-chemical changes resemble very high temperature reactions. Further, it has been shown by Trautz [1] that a class of photo-chemical changes—principally photolytically induced autoxidations—which are red-sensitive, have a very considerable temperature-coefficient, *e.g.* 2 to 3.

As a further argument in favour of this view, Weigert instances the order of these reactions, which, on due correction for the absorption of light (*vide* p. 218) is usually found to be unity—that is, that of a monomolecular reaction. But, as has already been indicated, this is often only true for a certain period of the reaction, and by arbitrary disregard, very often, of the anomalous "variable period." There was similarly a time when the uniform unilateral dispersion-curve of transparent bodies was supposed to exhibit the whole phenomenon of dispersion, prior to Kundt's and Christiansen's discovery of "anomalous dispersion" (*vide* p. 196). The discussion of "induction" (p. 275), on the lines of its analogy with electrodynamic induction, shows that an exponential formula $C = C_0 \left(1 - e^{-\frac{t}{\lambda}}\right)$ would probably hold for the current, or *reaction-wave* in the stages accessory to the installation of a *steady* value C_0.

Hence when C, the current, or rate of change, $= J\frac{\Delta x}{\Delta t}$, is sensibly uniform $= C_0$, the effect of self-induction is negligible. But with heterogeneous illumination, a considerable number of such initial phases, with different time-constants, are possible, and all these must conspire to achieve the uniform period, which is the resultant of a multitude of minor causes converging together in one *effect*. It is the effect which is uniform, and the rate of change of which, iso-dynamically, can often be represented by a monomolecular formula, but to regard this formula as the essence of the *genesis* of the reaction is to ignore the thousand and one minor obscure factors which

[1] *Zeit. wiss. Phot.*, **6**, 169 (1908).

contributed to it. In so far as concerns the *deduction period* of an intermediary complex, which may well be an adsorption-polytrope or polymere heterogeneous throughout with itself, of the kind postulated by Weigert, and which yields *principally* one well-marked chemical compound or a constant boiling mixture, such as $\frac{HCl}{H_2O}$, the monomolecular reaction-formula, taken inversely as

$$x = x_0 e^{-\frac{t}{\lambda}}$$

would obtain, and if the convergence-rate of the subsidiary "induction-lines" to form the (photo)-ferment or intermediary complex just balanced its rate of decay in the direction indicated, one would have the case of uniform formation of the product per unit time obtained with the chlorine-hydrogen actinometer under favourable conditions. But if the initial action of light consist in atomizing, and perhaps indeed, in sub-atomizing an original molecular complex, one would have equal reason to assert that, *qualitatively*, considering the heterogenesis first effected, the photolytic reaction was initially of indefinite order theoretically approaching ∞ both positively and negatively, but *quantitatively* of order practically approaching unity. But this unity would be rather of the micellar aggregate, the quite specific but heterogeneous crowd or cloud of molecules yielding a hylotropic phase to the depolarizing, measuring, or indicating meter, than of any qualitatively unique single molecule *in medias res*, in the process of transition.

As expressing approximately the law of change in these reaction-shells, Weigert suggests the formula—

$$v = \frac{\Delta x}{\Delta t} = \frac{SDn}{\delta}(p - p')$$

Here S is a constant expressing the combined influences of the actual volume of the gas-phase, the magnitude and other properties of the nuclei or micellæ, n, the number of active gas-molecules reacting per shell, and, depending upon the concentration of chlorine and the absorption of light, D the mean diffusion-coefficient of the gas, $p - p' = \Delta p$, the

pressure-difference under which it enters the shell, and δ the thickness of the shell.

If we suppose that the shell adjusts its mean cohesion-pressure, p, to correspond to an average thickness δ, it appears that this last can be but little different from the wave-length of the reaction-wave in the system, supposed to be stationary in the steady state, and it becomes probable that the kinetics of photo-chemical change will be found to have considerable affinity with those of explosion-waves.

As remarked, this view assumes that in photo-chlorinations, it is generally the chlorine which is specifically light-sensitive alone, in virtue of its absorption of light; this process involves a variation of state of the chlorine, an idio-chemical change, resulting in the segregation of a *more* condensed phase dispersed throughout a *less* condensed phase, these terms referred relatively to the *status quo ante* dissociated by light. Left to itself, on removal of light, this state of affairs would tend to readjust the prior equilibrium, but in the presence of other substances the proto-nuclei due to such a single wave of shock may be partly conserved, though at the cost of inception of reaction with the subsidiary bodies. It is this variable period of intermediate adsorption which occasions the phenomena of induction, and which is not, perhaps, ever representable by any finite number of chemical and mathematical equations, although it might perhaps be possible to express the adsorption-reaction-isochore for a finite number of purified components by a unique function of a family of curvilinear integrals.

That may be perhaps a task for the future. The actual influence of the activated chlorine upon other substances may be figured to some extent as follows. We have already referred to the interfacial tension of the capillary layer of pure bodies.[1] The notion of a dislocation by a light impulse of a prior homogeneous state of the chlorine implies a force of restitution in the parts dissociated coming more into play as the exciting force is cut off. If we suppose, as seems probable, that there must be, through the mass of chlorine in the critically heterogeneous condition, zones of equipotential

[1] *Loc. cit.*, p. 285.

values of the interfacial tension, and, indeed, distributed in maxima and minima of this, it is the complex plane where this is a maximum that the induced reaction would be consummated with the greatest velocity, at the cost of retarding the return of the chlorine to its prior condition, to which, once a pulse of radiant energy has disintegrated it, it can only asymptotically approach. Any portion of a medium in this state, properly distinguished by the synergy or mutual energy of its co-existent heterogeneous phases, rather than the intrinsic energy of either phase singly, may be termed a synergid, a photo-couple analogous to a thermo-couple, and corresponding to some extent with Weigert's photo-ferments. It must tend, any such synergid transferred from its original locus, to spread the quality of strife, of conflict, of antagonism, of which it is a unit and in which it first came into being. All amphoteric bodies, such as amino-acids, which comprise both basic and acid functions in the same complex, would seem to be potentially "ferments,"[1] being calculated, in defect of extraneous residues, to become self-saturated or internally compensated, forming so-called "inner salts." At the same time, it is desirable to point out here that although the distinction drawn dividing processes of physical dissolution and diffusion of one phase of matter in and through another from processes of chemical interaction between different species is a practically valuable one, it is none the less, to a large extent, arbitrary and artificial; diffusion-coefficients and velocity-constants of chemical change being fundamentally correlative magnitudes, descriptive of the same change differently interpreted. This is recognized in the more recent modifications of the "solvate theory of solutions," in which it is recognized that the process of diffusion of salt or sugar in water is as much a chemical as a physical or mechanical process.

[1] On the principle that it takes two to make a quarrel. An amino-acid is obviously a duad, a contradiction in terms.

§ 112. Photo-ferments and Photo-sensitizing.

From the fact that insolated chlorine can facilitate the decomposition of $COCl_2$, Weigert argued that it should be possible to sensitize other gas-reactions not normally sensitive to ordinary light. Actually he found that the following reactions could be so infected :—

(i.) *Gas-reactions.*

I. Decomposition of ozone :—

$$2O_3 = 3O_2$$

System.	Condition.	Ozone on analysis.
Ozone alone	Dark	3·4–6·1 per cent.
Ozone alone	Light	3·45–8·3 ,, ,,
Ozone + chlorine . .	Dark	8·2, 10 ,, ,,
Ozone + chlorine . .	Light	0·0, 0·0 ,, ,,

II. Union of H_2 and O_2 to water.

Baker[1] found that this reaction is very slightly sensitive to ordinary light, moist explosive gas gradually combining after some months exposure to sunlight.

Weigert obtained, in the presence of Cl_2, 37–45 per cent. water on relatively brief exposure. Whilst it is possible that there is a complex intermediate cycle, in which ozone and ozonides of hydrogen, as H_2O_2, H_2O_3 may occur, it appears improbable that the cycle is by the steps

$$Cl_2 + H_2 = 2HCl$$
$$O_2 + 4HCl = 2H_2O + Cl_2$$

both from direct experiment to test this hypothesis, and the unlikelihood of a preferential action of chlorine on hydrogen in the presence of oxygen, which hinders that reaction.

III. Union of SO_2 and O_2 to SO_3.

Coehn[2] has shown that this reaction is sensitive to quartz-permeable ultra-violet rays, but not to those passing glass. In

[1] *Proc. Chem. Soc.*, **18**, 40 (1902).
[2] *Jahrb. Radio. akti.*, **7**, 577 (1911).

the presence of chlorine, Weigert effected the reaction in glass vessels in ordinary light. Sulphuryl chloride SO_2Cl_2 was formed to some extent at the same time.

IV. Union of N_2 and H_2 to ammonia.

A slight fixation of nitrogen to ammonia was effected by light in the presence of chlorine.

V. Oxidation of HCl (Deacon process).

Weigert suggests that this sensitizing of reactions not in themselves light-sensitive, at any rate to ordinary light, is contributory to the induction period. The inhibiting action of oxygen is possibly due to primary oxide-formation (water in the case of $H_2 + Cl_2$, CO_2 in the case of phosgene) about the nuclei, which prevents further action. This would be analogous to the "poisoning" of colloid metals by substances such as hydrocyanic acid, iodine, etc.

(ii.) *Photo-sensitizing of Solutions and Solids.*

The formation of such specific photo-ferments may be applied to photolysis in other than gaseous systems. It applies to an observation made by Kistiakowski.[1] He found that H_2O_2 solution, which in a pure condition, is transparent and stable in light, is rapidly decomposed by light in the presence of the photo-sensitive ferro- and ferri-cyanides. So far the behaviour is similar to the Eder solution. But further it was observed that only a brief exposure was necessary to induce a change which continued for some hours afterward. The reaction is of the first order, whereas, according to the equation

$$2H_2O_2 \rightleftharpoons 2H_2O + O_2$$

it should be of the second. The phenomena are explainable on the view that light forms a colloid ferment, which continues the decomposition catalytically. According to Haber, this body is principally a per-hydroxide of iron, $Fe(OH)_5$. A similarly continuing after-action incited by light is found in the action of light on bichromated gelatine. The insolubilization of

[1] *Zeit. Phys. Chem.*, **35**, 431 (1900).

the gelatine effected spreads or extends after cessation of exposure. Weigert applies the idea to a large number of photographic reactions, the photo-ferments being in his view the photographic "latent images," and having greater persistence in solid media. We may connect with this the peculiarities of the silver halides in the matter of light-sensitiveness, silver iodide being the most susceptible to light in regard to additive development,[1] the least if subtractive development is attempted.

The photo-catalytic decomposition of ozone by light and chlorine was investigated more closely by Weigert, and his results are interesting as showing both the artificiality of the distinction made between optical and chemical sensitizing, and throwing more light on the mode of it. The terms were originally used by H. W. Vogel,[2] the one, chemical sensitizing, to describe the supposed function, *e.g.* of gelatine in silver halide-emulsions as a receiver of split-off halogen, the other, the effect of certain dye-stuffs in small quantities of making the halides sensitive to the more refrangible rays. As Winther's investigation on the Eder's solution shows, the optical behaviour of the sensitizer cannot be absolutely separated from its chemical activity.

Ozone and chlorine were mixed together in a thin glass bulb connected with a manometer charged with strong sulphuric acid, and the course of the reaction followed by the variation of pressure consequent on the transition $2O_3 = 3O_2$. The results were as follows :—

(*a*) Course of the reaction, *vide* Fig. 41. In darkness, the pressure remains constant ; on illumination it increases in linear proportion to the time, the velocity increasing on approaching the illuminant, decreasing on withdrawing it. On cutting off the light the pressure reached fell slightly, then remained constant (*vide* Fig. 41). When the ozone is exhausted, the reaction stops abruptly, but curiously enough, just before this conclusion the pressure suddenly jumped.

(*b*) The velocity was independent of the concentration of

[1] Sometimes termed "physical development" in contradistinction to "chemical," but it really consists in the use of an auxiliary silver solution.

[2] Cf. J. M. Eder, *Handbuch d. Phot.*, I. 45 (1906).

ozone. Compare the polymerization of anthracene by light (p. 220).

(*c*) The velocity increased with the concentration of chlorine, but not in direct proportion.

TABLE XXIII.

Vol. % of Cl_2	4·7	7·2	11·3	15·2	23·4	28·5	48·7	70·0	
Velocity $= \frac{\Delta p}{\Delta t}$	16·0	23·4	24·0	32·5	32·5	36·5	40·0	43·0	$\times 10^{-2}$

(*d*) The reaction-velocity is nearly proportional to the *intensity* of the light. A mercury arc was used, the rays

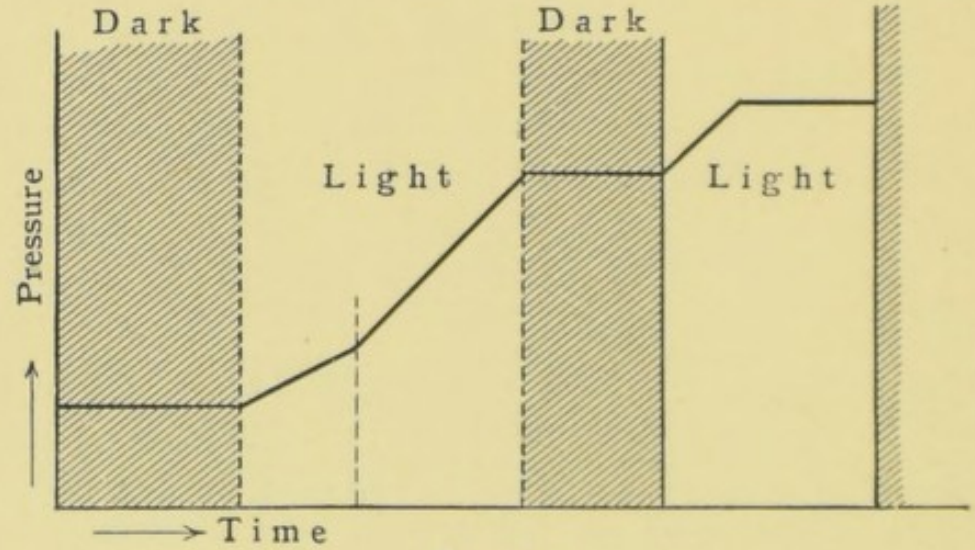


FIG. 41.

between 365 and 405 $\mu\mu$ being the ones chiefly effective. Hence, one reaction-vessel could be used as an actinometer to determine the absorption in another.

TABLE XXIV.

Chlorine per cent.	10	20	30	40	50	60	70	90	per volume.
Light absorbed .	47	72	86	92	96	80	99	100	per cent.

Comparison of these figures with the table for the velocities and chlorine concentrations shows that the velocity

is directly proportional to the light absorbed by the chlorine, being given by the formula

$$v = \frac{\Delta p}{\Delta t} = a(1 - e^{-k\epsilon})$$

where a is a constant, k the concentration of chlorine, and ϵ the extinction-coefficient. Hence the "optical" and chemical absorptions are directly proportional to each other.

(*e*) The temperature-coefficient was small, 1·17 to 1·26 between 15° C. and 45° C., but at 45° thermal dissociation of ozone commences.

In apparent contradiction to Weigert's theory of reaction-nuclei is the fact that the velocity measured is, like that of the polymerization of anthracene, independent of the amount of the disappearing phase. On the theory of diffusion (p. 304) of this into the shells of influence of the nuclei, the velocity should have been of the first order as regards ozone, whereas it is actually of zero order. But, as pointed out in the discussion of the conception of photo-ferments, not only is the distinction between diffusion and chemical change one not always capable of precision—these being two ways of considering the same process on different planes of interest—but it is rather the active photo-ferment which pervades the resting gas-phase,[1] so that any eventual chemical decomposition of this last occurs in a plane wave-front, and independently of the total mass of substance decomposable, as in an electrolysis or other heterogeneous reaction when polarization is eliminated. If only a finite number of nuclei were formed for a given measure of radiation, then the limited number of chlorine nuclei working at full tension determine the rate of change. An illustration may make clearer this independence of the velocity of the amount of ozone. Suppose a limited number of executioners at work, and a certain number of victims presented for decapitation. Let the executioners operate at their maximum efficiency, then in the steady state, the rate of decapitation will be independent of the number of victims to be executed, these being kept passive by the executioner's

[1] Cf. the photo-dromic processes instanced on p. 323.

supporters. In effect, any excess of victims might conceivably embarass the execution party, lessen the efficiency, and diminish the reaction-velocity. A similar example would be a shaving saloon. The rate of conversion of unshaven into shaven customers would only depend to a very slight extent upon the actual number of unshaven customers presented, it would be directly proportional to the number and efficiencies of the intermediate complex (barber ~ shavee), which would exist only in actuality during the reaction and as the reaction-nucleus, and the cessation of which, supposing the activity of the barber, like that of chlorine in light, to be maintained constant, would coincide abruptly with the exhaustion of a batch of clients.

Whilst the explanation of the ultimate mechanism of actual photo-chemical metathesis is still to seek, it seems feasible, from the known influence of certain rays in the ultra-violet and infra-red upon the decomposition of ozone that when chlorine is excited by light it emits a fluorescence or luminescence spectrum containing rays which affect the immediately contiguous ozone, or other such substance drawn into its interfacial plane. As we shall see later, there is a close relation between the fluorescence or luminescence spectrum of elements and their absorption spectrum, and that its nature is modified by the presence of small amounts of other substances.

CHAPTER VIII

SPECIAL PHOTO-CHEMISTRY

§ 113. Photo-chemistry of the Other Halogens.

It is fully in accord with the onus of the Periodic Law that insolated chlorine approaches, in its altered behaviour and increased reactivity, to fluorine. Practically nothing is known of the photo-chemical capacity of this latter element in the uncombined state, and indeed, the difficulty with this element is not to encourage it to react but to hinder it and find suitably indifferent receptacles. What is interesting, then, is the marked indifference of fluorine compounds to light. Silver fluoride, noticeable already for its much greater solubility in water compared with the other silver halides, is not distinguished by any particular light-sensitiveness, whilst the remarkable transparency of fluor-spar for the invisible spectrum is evidence of the imperturbability of the chemical equilibrium conferred by fluorine when subjected to rays generally all potent to dissociate. On the other hand, bromine and iodine are both sensitive to light and their reactions greatly affected by it, in correspondence with the strong absorptions they exhibit. This photo-sensitiveness persists to a greater or lesser extent in the compounds of these elements with others. If we may compare the tendency of an element to form stable self-combination phases—Graham's idio-chemical attraction—with what is termed electrically, self-induction (*vide* p. 275), this tendency is evidently more marked in the halogen series as we proceed from fluorine to iodine. In effect, the increase of atomic weight in this direction is only one mode in which the same tendency is manifested. A very general distinction between the behaviour

of bromine in regard to its action on aromatic bodies with side-chains is found according as the reaction is allowed to take place in weak (white)-light (or darkness), or in intense (white)-light. In the former case, bromine is substituted for hydrogen in the aromatic nucleus, as

$$C_6H_5.CH_3 + Br_2 \rightarrow C_6H_4Br.CH_3 + HBr$$
in weak light and darkness

in the latter, the substitution is in the side-chain

$$C_6H_5.CH_3 + Br_2 \rightarrow C_6H_5.CH_2Br + HBr$$

a difference which is found for a whole series of alkyl-benzene bodies.[1]

According to Beilstein, this same difference in behaviour is found according as bromination is carried out in a cold liquid or in the vapour of boiling hydrocarbons. Even in this case, the difference may depend upon a photo-chemical action, for if traces of oxygen were present in the hydrocarbons, a transient chemi-luminescence might occur.

Solutions of bromine in water (bromine water) are sensitive to light, but not so markedly as those of chlorine. The reversible reaction—

$$Br_2 + H_2O \rightleftharpoons HBrO + HBr$$

is one which can occur in this case, whilst the photolytically influenced reactions

$$2HBrO \rightleftharpoons 2HBr + O_2$$
$$2HBr \rightleftharpoons H_2 + Br_2$$

could concur in establishing a cycle regenerating *bromine*, as photo-catalyst, whilst furthering both oxidation and reduction reactions concomitantly. But more experiment upon the photo-chemical capacities of the three-component system—

Bromine | Water | Receptor

are required.[2] Of the salts of bromine with metals, silver

[1] J. H. Schramm, *Liebig's Ann.*, **18**, 350, 606, 1272 (1885); *Monatsheft*, **9**, 842 (1888).

[2] Cf. Witwer, *Pogg. Ann.*, **97**, 304 (1856); and Pedler, *Trans. Chem. Soc.*, **57**, 613.

bromide occupies a peculiarly important place, as the chief basis of photographic emulsions.

Iodine is remarkable for giving different molecular weights in different solvents, and generally in exhibiting a wide range of variation of its self-induction or power of association, which is also a function of the radiation-field it is exposed to. The condensation of iodine vapour from hydriodic acid when a beam of intense light is passed through this was observed by Tyndall in the course of his researches on radiant heat. It should be noticed that solutions of iodine show marked selective transmission and absorption in the infra-red spectrum. Coblentz[1] has investigated the colour and absorption over a wide range of conditions, with results as follows. Iodine forms either brown or violet solutions, characterized by differences in the molecular weight and degree of association. The brown solutions in chloroform, carbon di-sulphide, alcohol and acetic acid transmit the red end of the spectrum, but show strong absorption in the violet, the converse being the case with *violet* solutions. The solution in carbon di-sulphide has an absorption maximum at 500 $\mu\mu$ and transmission beyond 1100 $\mu\mu$. The brown solutions in alcohol have a maximum absorption from 1400 $\mu\mu$ to 3000 $\mu\mu$ and then become transparent again.

Iodine, like certain organic dye-stuffs,[2] can form true solutions or "colloid" solutions of many degrees and grades. (It is convenient to distinguish true solutions from colloid solutions, but it should be remembered that they merge imperceptibly. A colloid dispersion or pseudo-solution, termed a "sol," is generally in adsorption-equilibrium, *i.e.* fluctuating equilibrium with true solutions of its constituents, *i.e.* with its ambient medium.) The nature of the poly-iodides formed by the alkali metals, and which may be considered as correlative to the idio-chemical attraction of iodine atoms for each other has been investigated by H. M. Dawson.[3] This example of condensation effected through stimulation of the residual affinities of an element may be regarded as foreshadowing to

[1] *Phys. Rev.*, **16**, 35, 72 (1902) ; **17**, 51 (1903).
[2] Cf. S. E. Sheppard, *Proc. Roy. Soc.*
[3] *Trans. Chem. Soc.*, **7**, 46 (1903).

some extent the well-known coagulative effect exercised by many electrolytes upon colloids. It appears natural to assume that the affinity acting between atoms of the same element is rather different in degree than in nature from that acting between atoms of different elements, just as in the theory of electro-dynamics self-induction is regarded as similar in nature to mutual induction. Further it appears probable that this affinity is a stress alternating between repulsion and attraction, the virtual tendency to either convergence or divergence of affinities being made definite and real, in one sense or the other, by the introduction of a trace at least of a chemically different element, more or less independently of mechanical conditions of temperature and pressure, although these of course must influence the action, and particularly by facilitating or impeding the introduction of the essential catalyst, the "analytical impurity" necessary for real synergy and synthesis. This problem seems most open to attack through the study of the action of "corpuscular" radiations upon carefully purified elements, and by the spectroscopic examination of the effect of selected monochromatic rays upon purified elements brought to a radiant state (*vide* p. 413).

The photo-chemical behaviour of hydriodic acid has already been discussed (p. 208), whilst that of silver iodide will be considered shortly (p. 371).

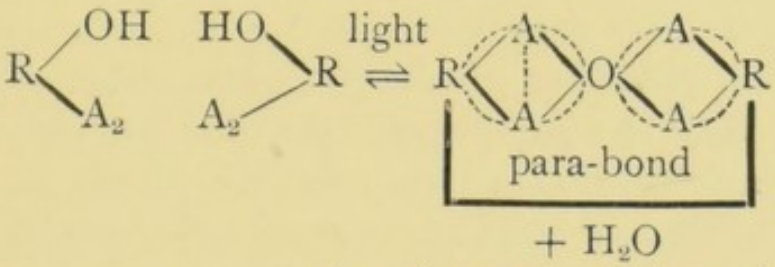
§ 114. Photo-sensitiveness of Salts of Metals.

The greater proportion of ordinary crystallizable salts of the metals, whether in the solid state or dissolved, are comparatively stable in respect to light. But this stability is certainly relative rather than absolute, being an inverse function of the *absorption* of light of the bodies, and is, practically, not disconnected with the fact that it is rare for these bodies to be exposed without intermission to light. Wherever a substance exhibits a characteristic selective absorption of light, this may be regarded as evidence of *virtual* intra-atomic changes of valency, which only require accentuating in one direction to yield a permanent alteration of equilibrium, an actual as distinct from a virtual change.

It has been observed that aqueous solutions of the salts of the heavier, polyvalent metals undergo a gradual change of character on keeping. This change is apparently of the nature of a hydrolytic cleavage of the metal salt, leading by a series of reactions in stages, with concomitant side-reactions *fixing* each stage enduringly and irreversibly as evolved, to the deposition of structurally conformed aggregates of insoluble oxides, sulphides, and ternary and quaternary complexes of varying composition. It is suggested that this kind of change is furthered by light, influencing in the direction from left to right changes partially representable by such equations as :—

I. $$RA_3 + H_2O \overset{\text{light}}{\rightleftharpoons} R(OH)A_2 + HA \uparrow \text{ (volatile acid)}$$

i.e. heavy hydroxy salt

II. 

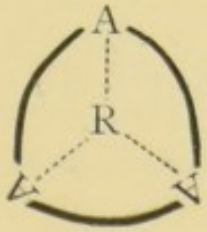
$+ H_2O$

i.e. photo-anhydride and water.

I. expresses the direct reaction between water and the salt, the *solvation*, and

II. the consequent reaction between hydroxy-salt molecules, the *coagulation* in which *water* is regenerated, whilst an *anhydride* is formed through the concomitant development of the residual affinities both of oxygen and of the acid radicle of the original salt. *Valency* is shown in the continuous lines, *contra-valency* in the dotted lines.

Supposing the original structural unit for the salt RA_3, R being the positive, A the negative component, to be represented *in plano* by—



for a single crystallogenic unit of the triclinic[1] system; the *ionizable* (contra)-valencies of the hetero-chemical union between the basic and acidic constituents being denoted by the straight, discontinuous or broken lines, the non-ionizable valency of the homo-chemical union between the acidic constituents by the continuous curved lines. In a solid state the R's may be conceived as similarly united by bonds of homo-chemical union traversing the plane of the paper, *i.e.* normal to the plane of the A's, and also, in the static equilibrium of the crystalline condition, forming closed circuits in turn, so that the distribution of affinity is thus *solenoidal* throughout, there being chemo-static equipartition of the affinity of the system, its "potential" (Gibbs) between the self-reciprocal linkings between identical atoms and the self-conjugate linkings between dissimilar ones (ionizable valencies).

A solid, *i.e.* a *dense* aggregate of such units will be composed of co-axial minor aggregates, having rings of *varying* numbers of the R's united in self-closed circuits, these circuli being of stability varying α-periodically[2] with the number, odd or even, thus united by idio-chemical affinity. It will be evident that the dissolution of such an *ensemble* (which, according to the numeration of the R-rings, may be equally *dense* everywhere or differentially *dense* in different directions) in a solvent must necessarily take *time*, depending, as it must, upon a displacement of the balance of affinity, of its static equipartition or equilibrium between the homo-chemical insulating circuits and the hetero-chemical conducting circuits. Hence this dissolution will proceed in a more or less pronouncedly

[1] For the sake of example. It is the essence of a crystalline system that it is self-similar throughout, *i.e.* its unit particles are projective images of its totality or ensemble. Hence, although a crystal increases its bulk by direct addition of self-similar units (*apposition* as *distinct* from *assimilation*), this growth in mere bulk is regulated by an *orientation* or vectorial factor, by the necessity of the *bulk* to conform as far as possibly to the true equilibrium-*shape* inherent in the crystallogenic units, and to which actual crystals approach in the measure that they are permitted to form under the play of inherent molecular forces alone.

[2] α being an algebraic number, in the more general case of other than simple harmonic motion.

step-wise manner, approaching a change by discontinuous jumps, regularly or irregularly scanned, according as the variability, throughout the *ensemble*, of the *numeration-factor* of the R's in ring-formation is small or large. For example, if only 4-membered R rings were present, it would be regular and simple, if 2, 4, 6, 8, etc., regular, but complex, necessarily with some kind of super-periodicity regulating the complex regularity. But supposing that there were *irregularity* intrinsically adjustable among the R's, we should then have, at the limit, approach of the process to a *dissolution* according to a *continuous function*.[1]

It must be remembered that the influence of a solvent cuts both ways, that is, it affects the nature of the solid form possibly crystallizing out, the variability of the ring-formation being a function both of the RA_3's and of the solvent. For, in the limit, we can conceive the binary complex RA_3 as a peculiarly permanent mutual solution of the R's by the A's, and conversely, its stability determined by a function of the mutual energy of co-existence of antithetical positive and negative elements. This mutual energy permeating the (theoretically) "dead" space between the atomic centres of activity is what we have termed "radiant energy," and may sometimes be evinced in visible form, as light, *e.g.* in the dissolution of certain compounds, a phenomenon termed *lyo-luminescence*. In this way, the process of dissolution of these salts may be regarded as really a very slow process, a slow, irreversible process leading to the formation of peculiarly stable photo-anhydrides or internal oxides of the elements, by way of series of very *rapid* processes, rapid *reversible* processes virtually, but *irreversibly* oriented actually. And all that only as a phase in the cycle of oxygen between a comparatively free, loosely combined state, and a bound, earth-bound condition. The formation of such photo-anhydrides would proceed then continuously in the direction of occlusion of oxygen in one direction, of hydrogen in another.

This notion of *structural metamorphosis* as intimately

[1] The view sketched in the foregoing takes into account the phenomena of *corrosion* and *peptisation*, as well as ordinary solution.

consequent with photo-chemical change marks the most important direction of photo-chemistry, that by which its data and dicta lead by way of colloid chemistry to the region of bio-chemistry. The physico-chemistry of colloid matter, the preliminary to the physiological chemistry of living matter, centres in the fact of the isodynamism of acidic and basic, oxidizing and reducing, functions, in one and the same uniquely specific complex, which possess a superior degree of dynamic meta-stability, and intrinsic variability of, so to say, temperament, consequent with the mutual *suspense* or *inhibition* of at least *two* conjugated binary systems [1] each tending to relax to a static crystalline state, but, these being geometrically incompatible with each other, actually the body and anti-body in question can but maintain an antagonism, an enduring strife, which keeps a pulsation of the affinity at work, and efficiently causes the destruction, whenever approached, of the *static equipartition* of affinity between *hetero-* and *homo*-chemical unions. It is this kind of *stress* peculiar to a nucleus of intrinsic strain that we have already regarded, terming it "synergy," as fundamentally characteristic of photo-ferments (*vide* p. 294). The self-same dynamic incompatibility it is which, *hindering* in complex organic bodies the easy crystallization of stable *solids*, facilitates conversely the easy coagulation of meta-stable *gels*. In consequence with this *dividuality* quite *specifically* superimposable on any aggregate of degree $i > 1$ of *kinds* of dual or binary molecules, superimposable like a sort of *imperium in imperio* on the generic duality of chemical elements taken *en masse* which is the central and cardinal fact for the stoichiometric chemistry of crystallizable matter, *colloids* are never in static but in dynamic, fluctuating equi-poise with the radiant energies of their circumambient medium. Each fluctuation of this initiates an impression, originally a pure strain, on the colloid which tends to develop and fix it, so to say, crystallographically, corresponding to a relaxation of the super-tension of its intrinsic internal dynamic incompatibility, but can usually only do so at the most transiently, partially, so antagonistic, mutually interfering, on an average, are the fluctuations of the

[1] The half-components of a double salt or reciprocal salt-pair.

ambient medium. But, for all that the partial fluctuations are virtual, reversible, and self-compensated, there is ever in time an orientation which conforms a *series* of such reversible reactions to real irreversible change. There arrives in time, by a consummation of such partial movements of relaxation, of such impressions, an epoch when the super-tension of matter in the colloid state, the mutual super-saturation of the alternative factors of the mass of heterogeneous binaries, relaxes, and it has irreversibly to dissipate its superfluity of free energy, revealing a quasi-static structure embodying the past history of the synergy of forces that made it. Wherever there is matter in the colloid state, fluctuations of radiant energy are inscribing signatures upon it of the irreversibly propagated periods of stress and strain of the aether of space. The structures evident are only for the most part rough drafts, crude sketches preliminary, so to say, to the real morphogenesis which nature practises in the organic world, where the *specificity* or idiosyncrasy characteristic of the reactions of matter in the colloid state is cumulatively presented and compounded in the individuality of living organisms.

In connection with the relation of light to the adjustment of matter between colloid and crystalloid states respectively, it is appropriate to mention the so-called molecular alterations produced by light, phototropic modifications of the state of aggregation, photo-mechanical deformations and disintegrations and positive and negative helio-tropisms (mass-movements) of crystals.[1] These may be regarded as integral resultants of true photo-chemical changes.

[1] Crystals of many substances are disintegrated and sublimed by light when exposed in closed transparent vessels, being generally deposited on the better illuminated side (cf. J. M. Eder, *Handbuch d. Phot.*, I, 123 (1906), and particularly P. N. Raikow, *Chem. Centr. bl.*, **2**, 1392 (1902)), often in rimes like the vegetation figures of hoar-frost. K. Schaum (Eder's *Jahrb. f. Phot.*, 1905) considers that air-currents play a considerable part in influencing such transvection. But, no doubt, such thermo-taxes and chemo-taxes are both concomitant with the propagation of light, and the disputes as to whether some permanent alteration in matter induced by light is mechanical or chemical are mostly sterile. We may say that all compounds of the metals are potentially sensitive to radiations of some order.

§ 115. Phototropy of Silver Compounds.

But whilst such changes are usually too slow to be practically useful, there is one metal which offers almost a plethora of phenomena in the actinotropy of its compounds, namely *silver*. Although the term "phototropy" was originally used for the oscillatory changes in light of different refrangibility shown by certain organic bodies, notably the fulgides (*vide* p. 338), this phenomenon, better termed *chromatropy* or colour-adjustment, was previously observed for silver compounds. The literature on this subject is extremely voluminous, very scattered and of very unequal value, so that only the historically important references will be cited. The change which "horn-silver" or fused silver chloride undergoes in light was observed by Scheele (*vide* Chap. I.), and it was subsequently found that this was chiefly produced by the rays of low refrangibility. Seebeck[1] in 1810 found that freshly precipitated silver chloride exposed in a moist state on paper to a prismatic spectrum reproduced the spectral colours, though very imperfectly and impermanently. Red was well reproduced, yellow poorly, green as bright blue, blue well, violet with a purple tinge, and ultra-violet as lavender grey. Silver chloride after preliminary darkening in white light, gave the same result. This phenomenon remained unnoticed, till its study was revived by Ed. Becquerel,[2] to whose broadly inquisitive yet profoundly penetrating genius photo-chemistry owes so much. The subject was also studied by Sir John Herschel and Poitevin, but their work for some time served rather to obscure than to clarify this problem. Becquerel employed polished silver plates, which were halogenized to a slight thickness by electrolysis, the superfacies of halide being probably from 0·001 mm. to 0·002 mm. in depth. He found that after prolonged exposure such films reproduced the spectrum very fairly, but that this power of colour-reproduction vanished in darkness. A physical explanation of

[1] Goethe's *Farben-lehre.*

[2] *La lumière, ses causes et ses effets.*

these colours was put forward by Zenker,[1] who ascribed them to stationary waves. For a discussion of the formation of stationary waves, the reader is referred to text-books of physical optics and wave-motion. The essence of the phenomenon is the interference of the elements of an incident wave train impinging upon an optically denser medium with waves reflected back, which recoil retarded in phase by a sub-multiple of a wave-length.

In the medium immediately contiguous to the reflecting surface a stratification of the energy ensues, the loci where the kinetic energy is a minimum being termed "nodes," those where it is a maximum "anti-nodes." Supposing now that this kinetic energy of light to effect a photo-chemical change in the medium, it is obvious that the product would be formed in lamellæ of maximum and minimum densities separated by intervals commensurable with the wave-length of the light acting. If they are formed by spectrally dispersed rays, or, generally, by coloured light, the space-gratings thus created (and *fixed* by side-reactions of the type already instanced in the section on the formation of photo-anhydrides) will necessarily tend in *white* light to reproduce the colours which originated them. It is evident that the more completely this differentiation of the original medium is effected, and the more the initial substrate is finally converted and, so to say, assimilated to the acting light-images, the purer and more vivid will be the subsequent colour-reproduction. This principle was adopted by G. Lippmann[2] in his method of colour-photography, in which the posterior reflecting surface is a layer of mercury and the lamellarly distributed "latent image" is subsequently developed.

O. Wiener,[3] to whom we owe a very comprehensive critique of the various processes of photo-chromy, has shown that Zenker's view is correct for the colours with Becquerel films on metallically reflecting supports, since the colours seen in white light vary with the angle of viewing and the refraction

[1] *Lehrbuch d. Photochromie*, Berlin, 1868.
[2] *C. R.*, **112**, 274 (1891).
[3] *Ann. Phys.*, **45**, 237 (1895).

of the contiguous medium through which they are observed. But this does not hold for the colours obtained with Poitevin's preparations (he used oxidizing substances, such as bichromates, to increase the colour-sensitiveness of silver halides), and Seebeck's on other than metallically reflecting supports. The colours here cannot be referred to a total space-structure impressed in the film, but must inhere in the photo-product itself. They are produced by some kind of selective absorption, and are hence termed body-colours, as distinct from the colours of thin plates. To account for them, Wiener was led to a general theory of colour-adaptation, which may be said to form a bridge between the false (Schein-farben) diffraction and interference colours, and the true (Körper-farben) pigmentary colours.

§ 116. The Allotropy of Silver.

If the reduction of silver from its salts and compounds is variably retarded, a series of different modifications are obtained which have been termed allotropic.[1] Carey Lea, who first studied the question systematically, found that by suitable variation of the reduction-conditions, the following typical modifications were obtainable—

(*a*) Water-soluble silver, giving deep red solutions (or hydro-sols, which pass more or less rapidly to suspensions), lilac to blue-green as a moist coagulum, metallic blue-green when dried.

(*b*) Insoluble form obtained from the first. Dark reddish-brown when moist, similar to (*a*) when dried. The result of irreversible coagulation of (*a*).

(*c*) Golden silver, dark bronze when moist, like metallic gold when dried carefully.

Similar colloid silvers may be obtained by Bredig's method of electric disintegration.[2] An arc is passed between silver poles under water, which must be carefully purified and

[1] Cf. *Kolloidchemie u. Photographie*, Lüppo-Cramer, Dresden, 1908.

[2] Cf. A. Müller, *Allgem. Chemie d. Colloide*, p. 6 (1907), Barth, Leipzig.

rendered very slightly alkaline. These forms all dry readily on paper with their particles in optical contact, and pass readily under physico-chemical stimulus into the ordinary grey-white metallic silver. Carey Lea considered that this last is a highly polymerized form of silver, a view which agrees on the whole with its physico-chemical behaviour.

It is, however, questionable how far any of the disperse forms are pure silver, since it is recognized now that such colloids are intimately dependent upon traces of adsorbed electrolytes for the maintenance of their meta-stability. All the forms are light-sensitive. Carey Lea found that daylight converted the yellow or red modifications into the grey (passive) silver, whilst the blue-green and yellow-red forms are interconvertible according to the nature of the illumination.

On the other hand, there is evidence that metallic silver, in coherent plates, tends to disintegrate to some extent, at least in the presence of air and water,[1] yielding visible or latent images on controlled exposure.

§ 117. The Action of Light on Silver Salts.

The action of light upon the salts of silver, but particularly upon the halides, is of cardinal importance for photography. That the "blackening" or darkening of silver halides in light is in principle a reversible reaction was first quantitatively shown by R. Luther.[2] His method consisted in exposing silver bromide or silver chloride to a graduated series of quantities of illumination, the moist halide (free from gelatine) being exposed under a tube-photometer, a number of separated tubes having entrance-pupils for an even area of illumination in ratios increasing in the proportion of $1 : \sqrt{2}$, the uniform area of illumination being diffused daylight. The halide was in contact with a solution of halogen, and in this manner, by varying the concentration of the free halogen in the solution, it was possible to determine the corresponding values of the illumination

[1] J. W. Waterhouse, Eder's *Jahrb. f. Phot.*, p. 599 (1901), following older researches of Moser on the surface-changes of metals and glasses in light.

[2] *Zeit. phys. Chem.*, **30**, 628 (1899).

which was just counterbalanced by the halogen, this latter reforming the dissociated halide or just inhibiting, at equilibrium, the darkening. Luther found no simple relation—such as inverse proportionality—between the quantity of light or flux-density of illumination per unit area exposed and the inhibiting concentration of chlorine, which is probably connected with the fact that he used heterogeneous illumination. He concluded from further experiments that the invisible or "latent image" formed by light in the silver halides had the same chemical constitution as the visible image, and from measurements of the E.M.F. of halogenizing solutions which just

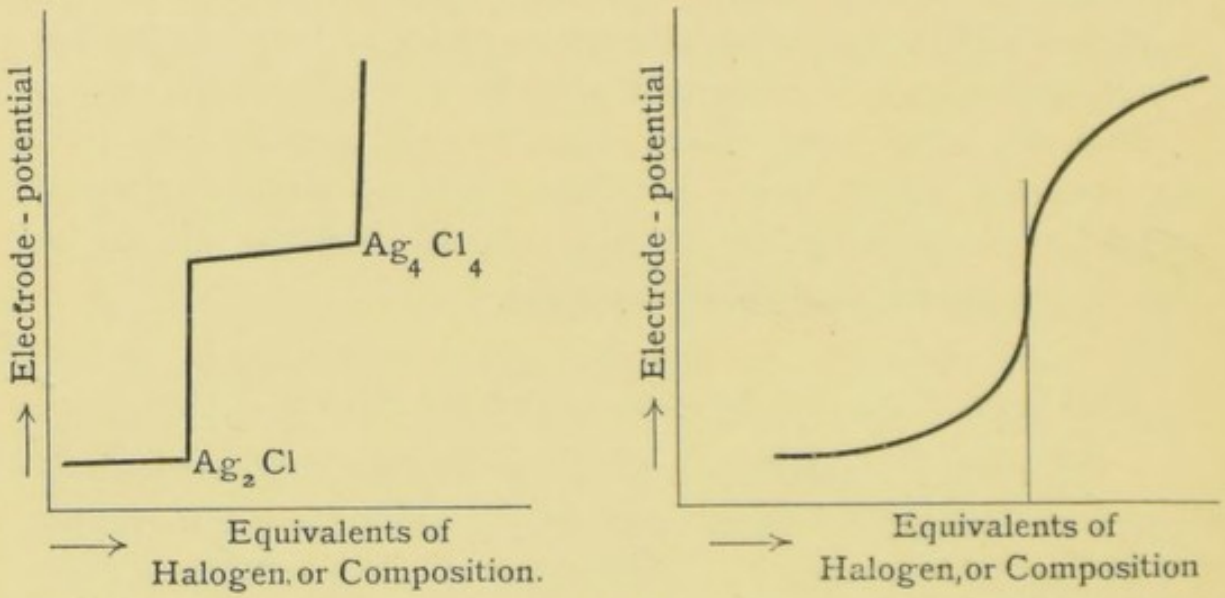


FIG. 42.

bleached the visible image, just destroyed the invisible image, that the constitution of this latter was that of a sub-halide, Ag_2Hal, in agreement with the opinion of Abney and a great number of investigators on the photographic process.

The principle employed in this latter discrimination of a stoichiometrical relation by a dynamic method may be diagrammatically illustrated as above.

The E.M.F. at a silver-halogen electrode, balanced against some "standard electrode" of known potential, is determined for increasing concentrations of halogen. As abscissæ are plotted equivalent of halogen per 100 equivalents of silver; as ordinates, values of the electrode-tension or stationary E.M.F. corresponding to compositions of silver and halogen.

Supposing the E.M.F. to vary by discontinuous jumps or steps, as shown in the left-hand figure, the existence of true equilibria corresponding to the compounds indicated may be inferred. On the other hand, if the potential changes *continuously*, as indicated in the right-hand figure, the existence of any such stages becomes more hypothetical. Now it is evident that there is a large measure of "false equilibration" possible here, according to the closeness of plotting and number of observations made, whilst on the other hand, sufficient *time* must be allowed at constant temperature for the system to adjust both *diffusion* and *electric equilibrium*. The problem is somewhat the same as that in the tensimetric determinations of the stoichiometrical composition of hydroxides.[1]

Subsequent investigations make it probable that the course of the curve of E.M.F. against composition is essentially and naturally different according to the nature of illumination of the system, certain definite compounds being provably existent in light, but non-existent in darkness.

The question has been further investigated by E. Baur, H. Heyer, and H. Weisz.[2] Baur mixed colloidal silver with determinate quantities of chlorine, and concluded that mixtures containing less than 50 equivalents of chlorine to 100 of silver were not colour sensitive, those containing more were. But this involves a *petitio principii*, as is evident from what has already been said upon the chromatropy of colloid silver itself. These are already pigments, and their colour-changes are necessarily less perceptible than those of a halide having greater percentage of white halide. On the other hand, Baur found that the potential of a silver photo-chloride electrode in normal KCl solution, admixed with a varying concentration of free halogen, and measured against that of a standard mercury-calomel electrode, varied continuously with the halogen-concentration. Hence, if any sub-halide exist, it must be capable of forming solid solutions or colloid complexes in all proportions with normal halide.

[1] Cf. *The Phase Rule*, A. Findlay, this series.

[2] E. Baur, *Zeit. physik. Chem.*, **45**, 613 (1903); H. Heyer, *Inaug. Dissert*, Leipzig, 1902; H. Weisz, *Zeit. physik. Chem.*, **54**, 305 (1906).

If the subhalide be capable of separate existence, eventually, as a metastable intermediate phase, the inequality

$$\Delta E_{\frac{Ag_2Cl}{AgCl}} > \Delta E_{\frac{Ag_2Cl}{Ag}}$$

should obtain ; that is, the potential difference correlative to the spring or transition of subchloride to chloride must be greater than that correlative to the transition of silver to subchloride. Both Luther's and Baur's conclusions lead to this notion.

Heyer made a series of measurements with carefully graduated halogen concentrations, and concluded as follows :—

(*a*) Mixtures of all potentials (which act at all) are capable of completely converting silver to normal silver halide (AgCl).

(*b*) When silver-subhalides prepared from Guntz's subfluoride of silver by metathesis with halides of the alkalies or of hydrogen were subjected to further halogenization, this was effected by solutions having the same potential as those immediately converting silver (Ag) to silver halide (AgCl). Luther's, Baur's, and Heyer's values for this oxidation-potential, reckoned for a concentration of chloridion of 10^{-5} per litre, corresponding to that of a saturated solution of AgCl in water, regarded as completely dissociated electrolytically are—

	Baur.	Heyer.	Luther.
π Ag → Ag_2Cl	−0·84	−0·84	−0·78
π Ag → AgCl	−0·99	−0·83	−1·23
π Ag_2Cl → AgCl	−1·14	−0·82	−1·68

Hence the existence of a half-halide of silver remains unproven in the cases of the chloride, the bromide and iodide, although the subfluoride separated by Guntz seems definite enough. But, considering the gradatim declension in optical and chemical properties of the elements—

Fluorine, chlorine, bromine, iodine,

it appears quite feasible that the existence of hemi-salts of these elements with silver would be contingent to the radiation-field. The study of alloys shows of itself how much greater, how many more in number, are the *possible* chemical combinations which may be plausibly alleged to exist, if only transiently

in *reality*, than the number which it is expeditious to distinguish practically. In fact, whereas the stable existence of a subfluoride is very probable, we shall see that in the case of the iodide of silver, under suitable radiation, the tendency of the photo-chemical reaction is rather in the direction of formation of per-iodides.

So far as the photo-chlorides and photo-bromides are concerned, a purely provisional explanation of their constitution is that they consist of "colloid complexes" or "adsorption compounds" of indeterminate proportions of "silver" associated with silver halide, with normal AgCl or AgBr.[1] As has already been pointed out, there are probably two independent but yet interfering processes in operation in the action of light upon most sensitive bodies. In the silver halides, we may consider one as the photo-mechanical modulation of the state of aggregation of chemically singular halide, a modulation of aggregation and disgregation of its crystalline conformation, typified by the reversible reaction

$$(\mathrm{AgHal})_m \rightleftharpoons (\mathrm{AgHal})_{m-n} + (\mathrm{AgHal})_n$$

the reaction from left to right being *heteroblastic*, corresponding to a disgregation of the crystalline units; that from right to left homeoblastic, corresponding to aggregation and increase in size of single crystal units. This reaction (or action and reaction) is *photo-mechanical*, its "go" is dependent upon the elastic stresses and strains experienced in the crystals, in their ellipsoids of elasticity, in the progress of polarization and diffraction of light, but it does not necessarily, but only contingently, imply any absolute segregation of the chemical molecule into its components. It is *photo-mechanically* and *thermo-dynamically* important, but not, directly, although indirectly, of *chemotaxic* moment. This *chemotaxis* is most probably essentially dependent upon the presence of foreign bodies, sensitizers, with which, sympathetically influenced by the action just instanced, actual *metathesis* takes place. It may only be water which is the sensitizing medium, but in that case, any colloid complexes of silver adsorbed to silver

[1] Lüppo-Cramer, *Kolloidchemie u. Photographie* (1908).

halide involve *definite* degrees of hydration of the halide, which *associated water* is simultaneously furnishing hydroxyl radicles to the "free" silver. There is an "ionization," for the actual heterogeneity of the tensions in such a condition involves the fact of electric charges of different sign on the micellæ formed, and there is probably an intermediate epoch of liberation and resorption of free oxygen correlative to any liberation and resorption of free halogen. This correlation will be dealt with particularly later, in the case where it had been most easily studied, that of silver iodide, owing to the greater inertia of iodine compared with bromine and chlorine, and the corresponding greater duration of the intermediate free periods.

If we take only water and air as the sensitizing media in this chemotaxis, the photo-chemical reaction proper, a large number of equations, all accurate enough for particular phases of the reaction might be written, expressing variable organizations of—

$$(AgCl),\ Ag(OH),\ (Cl_2)\ \text{sol. in}\ H_2O,$$

the formation and deformation of which would be syntonized with trains of vibrations of light absorbed, the photo-micellæ organizing according to the nature of the wave-forms incident in the sensitive mixture. Where other depolarizers than air and water are present, a greater variety of products is possible, and such reactions, though they may be termed *reversible virtually* or *in principle*, are in practice, in actuality, either irreversible or at the best pseudo-reversible. The photo-mechanical action aforementioned is to a large extent antagonistic to this chemotaxis, which tends to destroy the homogeneity of the crystallogenic units proper to the former, and to integrate *de facto* in body-colours, in definite chromoplasts, what in the pulsations of the crystallogenic units were only virtual and *de jure* shades and colours.

§ 118. Composition of the Photo-halides.

It cannot be said at present that it makes much practical difference whether the photo-halides be regarded as adsorption-compounds of silver with normal silver halide[1] in various

[1] With traces of silver oxides in some cases.

proportions depending upon dynamic factors of the field they are adaptations to, or as "solid solutions" in various, continuously varying proportions, of half-halide in normal halide of silver. Eder [1] prefers to consider them as intimate mixtures of the latter type, but having as general formula

$$Ag_mHal_{m-n}$$

(But, as we have remarked, there are probably traces at least of other elements present.) It has been shown by Carey Lea,[2] by E. Baur [3] and by Lüppo-Cramer [4] that similar bodies may be obtained by the following reactions:—

(*a*) Action of light on moist silver halide.

(*b*) Mixture of a hydrosol of silver with a hydrosol of silver halide, and addition of a coagulant—this being generally an acid.

(*c*) Slow or retarded chemical reduction of silver halide.

We are dealing here with aspects of change where three general conceptions intersect, namely, those of "chemical combination," "mechanical mixture," and "physical solution," and it is by no means an easy matter to decide which fits the facts observed most clearly. That in the cases where there has been shown to exist an analytic excess of silver over and above the proportion equivalent to the formation of AgCl, etc., in the photo-halides, this silver is not quite the same as ordinary metallic silver is evident from the resistance it offers to solution in nitric acid, it being practically impossible to remove the last 1 to 2 per cent. of excess.[5] Another observation leads to the same conclusion. Luther coated a portion of the interior of a glass tube with silver, another portion with silver bromide, sealed it up, and exposed the arrangement to light. The silver bromide darkened, and the bromine which was released attacked the silver mirror, turning it violet. Luther argues that it is thermo-dynamically impossible that in the enclosed system

[1] *Handbuch d. Photograph*, 1, 109 (1904).
[2] *Amer. Journ. Sci.*, 3, 33, 350.
[3] *Loc. cit.*, footnote.
[4] *Kolloidales Silber und Photographie.*
[5] Cf. J. M. Eder, *Handbuch d. Phot.*, 1, 239 (1906).

considered, metallic silver should be converted to silver bromide, whilst identically silver bromide is reduced to metallic silver, hence the inference that the product of light-action on silver halide, and the initial product of halogenization of silver must be a sub-halide. It is feasible, however, that the allotropy of silver should permit the development of forms optically heteromorphic yet thermally isodynamic. The theory has been sustained in regard to optical isomers in which not colour but polarization of light is the criterion.[1]

§ 119. Chromatropy of the Photo-halides, etc.

Apart from hypotheses, the photo-halides exhibit the property of adaptation of their body-colour to the colour of the incident light, reflecting blue principally when illuminated sufficiently long in blue light, and so on. Baur gives the following table as illustrating how far this property is influenced by the composition of the photo-halides.[2]

Table XXV.—Colour Reproduction by Photo-halides.

Per cent. of chlorine.	Transmission colour in bulk.	Transmission colour in film.	Reflection colour.	Solar spectrum rendering.
34·6	Absinthe	Bright yellow	Olive green	Nil
50·0	,,	,, ,,	,, ,,	,,
57·5	Yellow	Sienna	Dun brown	Correct, red poor
58·9	,,	,,	,, ,,	,, ,,
69·4	Orange	Fiery red	Chocolate	,, ,,
75·1	Purple red	Red violet	,,	Good
77·1	,,	Violet	Red brown	Very good
82·0	,,	,,	,, ,,	Red too purple, blue too dark
84·0	Rose red	Rose	Bluish rose	
87·2	Bluish red	Blue	Bluish red	
ex.95	Pink	Rose	Bluish rose	Very good
98	Lilac	Lilac	White to lilac	,,
99	Faint rose	Rose	Faint rose	

[1] Optically active bodies. Luther's argument requires homogeneous radiation. Actually, in heterogeneous radiation, there is an antagonism between different rays (*vide* p. 338).

[2] *Zeit. phys. Chem.*, **45**, 620 (1902).

It may be regarded as probable that, whatever be the nature of the photo-halides, similar products, in a suspended state of incipient dissociation, are formed in gelatino-halide emulsions.

With increasing excess of silver the sensitiveness and capacity for rendering colours diminishes; the pinkish preparations containing about 1 to 2 per cent. of excess silver are the most sensitive. Somewhat similar results were obtained by Wiener[1] using Poitevin's preparations. He groups the phenomena together under the general title of colour-adaptation (Farben-anpassung), and points out:—

There exist substances which exposure to illumination of definite hue causes to acquire the capacity of predominantly reflecting that hue. Wiener accounts for the production of these in a system capable of alternating between black, *i.e.* total absorption, and white, *i.e.* total reflection, as in the system silver ~ silver halide, on the ground of the mechanical principle of least action. In red light, red photo-chloride is formed, since it reflects red best, that is with minimum absorption and hence least action or change in the sensitive base. The stability of the red form is attuned to that of the field it is exposed to. This Wiener terms "mechanical adaptation" as distinct from the purposive adaptation of living creatures to their environment. Wiener points out that this automaticity, this existence of substances adapting their colours to the colours of the incident light, may help to make more intelligible, not so much the fortuitous factors in organic evolution, as the origin of the direct influence exerted by its environment upon living matter. Colour-adaptation is a well-known fact in biology. One will recall the chameleon, a beast apparently intended to point a moral or adorn a tale in proverbial philosophy. But investigation soon shows that the chameleon does not stand alone. Thus the pupæ of many, perhaps the majority, of Lepidoptera normally take the colour of their surroundings.[2] A definite chromatropic pigment was extracted by Poulton from the epidermis of

[1] *Wied. Ann.*, **69**, 488 (1899).

[2] Cf. *Die Grundlagen der Farben-photographie*, Sammlung, Die Wissenschaft, **14**, p. 59 (1906).

Amphidasis betularia, a species possessing a very elastic capacity of colour adaptation. The epidermis consists ofa dark outer pigment, beneath which there is present in fat-cells a green pigment, which is apparently the substrate of the dark pigment. This latter, like the "mixed black" of the modern photo-chromic processes with sensitive dye-mixtures,[1] degenerated in light into a wide range of hues, varying from black, blue-green, brown, green-grey to white, according to the illumination. This adaptation is capable of reproducing other colours than those normally presented to the organism under its natural conditions. Thus by suitable illumination Morris obtained white, red, black, and blue pupæ of *Danais chrysippus*, which are usually either pink or green.

Such facts, whilst of course illustrating the proposition that the boundary drawn scientifically between inorganic and organic beings, between non-living and living nature, is an artificial one, point to evidence for the Lamarckian view that the effort to adaptation on the part of an evolving organism is reciprocal to direct and causal influences emanating from the environment—*le milieu ambiant*, as Geoffrey St. Hilaire termed it—itself, and that the so-called bathmic factor, the primitive impulse to variation, which was all that Darwin required for the theory of natural selection, is not simply centred in the individual organism but conjugate with an extrinsic factor of a similar order, though it may be of different scale of duration, implicit in unorganized nature, which leads on the determination of metamorphic change.[2]

Fluctuations of their hue and texture under change of illumination are exhibited by many slightly soluble halides, sulphides, etc., of the metals. Calcium sulphide, CaS, changes colour,[3] mercuric sulphide[4] passes from red to black in

[1] Cf. *Die Grundlagen der Farben-photographie*, Sammlung, Die Wissenschaft, **14**, p. 59 (1906).

[2] On colour adaptation in living matter, see J. W. Wood, *Proc. Ent. Soc.*, 1869, p. 99; E. B. Poulton, "The Colour of Animals," 1890 (Kegan Paul, Trench & Co.); F. E. Beddard, "Animal Colouration" (London, 1895), p. 135.

[3] J. R. Mourelo, *Arch. sci. Phys. nat. nèer.* [4], **25**, 15 (1908).

[4] Cf. J. M. Eder, *Handbuch d. Photogr.*, **1**, 120 (1906).

sunlight, a change noticed by Pliny and Vitruvius; it is greatly affected by solvents and reversible by heat. Arsenic tri-sulphide, As_2S_3, is said to pass from a crystalline to an amorphous state; in connection with this the formation of thio-arsenates and arsenites, as well as of the colloid complexes studied by Linder and Picton,[1] should be considered. The iodides and oxides of mercury are also light-sensitive to some extent, as is cuprous iodide. These substances all give photo-electric effects (*vide* p. 361).

§ 120. Phototropy, etc., of Carbon Compounds.

The influence of light on carbon compounds is at least as intense at times and as extensive throughout as that which it has on inorganic materials. Of all the elements carbon seems to be the one which, somewhat paradoxically, exhibits the greatest inertia, the greatest energy, and the greatest entropy as regards radiant energy and light. It is only possible here to consider the interaction of light and carbon compounds at a few points. Baly's conception of isorropesis (p. 179), taken in conjunction with the experimentally evident correlation of dynamic isomerism with selective absorption, serves to indicate that the scope of a complete photo-chemistry of the carbon compounds would almost coincide with a general reaction-chemistry of these bodies. Hence we shall select the following points of particular interest :—

I. Phototropy of hetero-cyclic keto-bodies and of the fulgides.

II. Influence of light on stereo and dynamic isomerism of carbon compounds.

III. Photo-chemical bleaching of organic dye-stuffs and coloration of leuco-bodies.

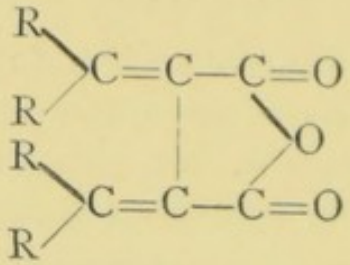
IV. Photo-chemical synthesis of organic compounds. Chlorophyll and photo-synthesis in plants.

Of these, sub-sections III. and IV. are considered after the chapters on photo-electricity, fluorescence, and chemi-luminescence.

[1] *Trans. Chem. Soc.*, **61**, 114 (1892).

I. Markwald first proposed the term "phototropy" to denote the behaviour of quino-quinoline hydrochloride, which passes from a transparent whitish condition in weak light to a strong yellow-green hue in intense light, the change reversing spontaneously in darkness, but more rapidly if heat be applied.[1] Similar, and even more remarkable, are the changes shown by the fulgides on variation of the light flux, which changes are better grouped under the term "chromatropy."

The fulgides are a class of dye-stuffs discovered and investigated by H. Stobbe.[2] Stobbe gives as the graphic formula typically representative of the group—



where R is a radicle, as hydrogen, or an aryl or acyl group.

These bodies, when exposed to light, undergo two kinds of change, one transient, reversible, and yielding the same chemical body; the other permanent, irreversible, and yielding quite different bodies. This second change is cumulative; it may be regarded as corresponding to a gradual fatigue, as the virtual or purely reversible change is more and more deficiently executed.

Thus if tri-phenyl-fulgide is powdered and placed between glass plates, after storage in darkness it appears at first orange-yellow in colour. Exposed to white light it goes brown, to blue light, black-brown. Investigation with a spectrum showed that the orange-yellow A-form is sensitive to blue and violet, *i.e.* to the rays it absorbs. The B-form thus produced is really blue; it absorbs orange, red, and infra-red rays, and is converted back by these into the A-form. This reverse change takes place only slowly in darkness, but may be accelerated some 1000 to 2000 times by heating. From the standpoint of the structure-theory of organic bodies it appears that the two forms are identical, although it is possible that some stereo-isomerism of

[1] *Zeitschr. phys. Chem.*, **30**, 140 (1899).

[2] *Lieb. Ann.*, **359**, 1–48 (1908).

the *syn*- and *anti*-type might fit the case. The two extreme modifications appear to form intermediate solid solutions in every proportion, and the actual equilibrium ratio at any moment depends upon the colour and intensity of the light the system is exposed to, as well as the temperature of surrounding media. Roughly speaking, we have the scheme

$$\text{A-form} \underset{\text{long waves}}{\overset{\text{short}}{\rightleftharpoons}} \text{B-form}$$

expressing such a chromatropic transition. In accordance with the principle of mobile actinic equilibrium, cases have been found of substances practically colourless in weak white light which give coloured bodies in stronger, more intense white light, which is due to the increasing proportion of rays of greater oscillation-frequency in the more intense light. Such is the case with *tetra-chlor-keto-naphthaline*, which is colourless in whole crystals, white when powdered, in weak light, but turns red-violet or purple in strong light, the exciting rays being chiefly in the extreme violet and neighbouring ultra-violet, as a quinine ray filter prevents this change. The exciting rays were found to lie between 359 $\mu\mu$–388 $\mu\mu$, the reversing rays from 514 $\mu\mu$–576 $\mu\mu$.

The results for three such bodies are—

TABLE XXVI.

Name.	Absorption of A-form.	Absorption of B-form.
Keto-naphthol	λ 388–350 $\mu\mu$ white or colourless	λ 576–514 $\mu\mu$ red-violet
Di-phenyl-fulgide	λ 510–436 $\mu\mu$ yellow-green	λ 625–510 $\mu\mu$ blue
Tri-phenyl-fulgide	λ 550–440 $\mu\mu$ orange	infra-red to 550 $\mu\mu$ blue

It will be seen that these substances all tend to follow the colour-adjustment principle enunciated by O. Wiener.[1] Two deductions are of interest :—

[1] *Loc. cit.*, p. 335.

(*a*) The exciting and reversing rays are mutually interdependent, *i.e.* are *specifically* antagonistic in regard to the given body, or in respect of the regulation of its constitution.

(*b*) Any displacement of the locus of the exciting group of rays towards the shorter or longer radiations, for another such substance, involves a corresponding displacement of the locus of the group of reversing rays.

Hence it is obvious that bodies might be isolated which would become coloured by absorbing infra-red rays, supposing a group of infra-red rays to be thus, in respect to the chemical potential of a certain substance, conjugate with a group of rays in the ultra-violet or to the visible region. In fact, such bodies as the double iodides of mercury and the alkali metals practically exemplify this, the coloration of which by heat-radiation may be used to map the equi-potential lines of flow of heat in a solid conductor.[1] Similar mobile chromatropic phenomena, involving the transient development (but without fixation or arrest) of dye-stuffs, may be observed with many isomeric keto-bodies of high molecular weight, and they overlap with the mutations to which Hantsch has given the general term *pantochromism*.[2] From the ketones we may take as example the photo- or rather chromatropic inter-conversion of the two stereo-isomeric *piperonylidine acetones*, or the photolysis of the *ortho*- and *para-benzylidene di-oxy p-benzoins*.[3] Of these the *ortho*-body is recognized as fluctuating between two phases

$$\underset{\text{dark yellow}}{\alpha\text{-ketone}} \rightleftharpoons \underset{\text{light yellow}}{\beta\text{-(iso)-ketone}}$$

whilst three inter-convertible phases have been assumed for the *para*-body

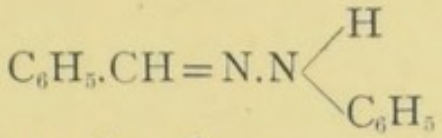
$$\text{(iso-ketone) } \beta \rightleftharpoons \gamma \text{ (allo-ketone)} \quad \text{in varying illumination } \overset{\alpha}{\rightleftharpoons}$$

[1] "Demonstration von Iso-thermen auf Platten," *Inaug. Diss.*, O. Hess (Marburg, 1906).

[2] A. Hantsch., *Ber.*, **44**, 1783 (1910); cf. *Ann. Reports Chem. Soc.*, **8**, 58 (1911).

[3] H. Stobbe and F. J. Wilson, *Ann. Chem.*, **374**, 237 (1910).

Similar behaviour has been observed with the *ozazones* and *hydrazones*. The *benzaldehyde phenyl-hydrazone*



fluctuates according to the scheme

u.v. and *violet*

Hydrazone A white to light yellow $\rightleftharpoons$ Hydrazone B red

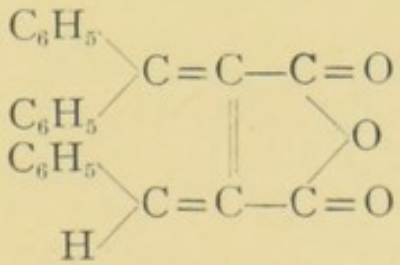
yellow

Obviously, in such cases, transient oxygen-occlusion and exclusion, with fugitive formation of *azo-dye-stuffs*, is quite within the bound of probability. This is supported by the fact that the virtual or reversible changes noted above cannot be indefinitely repeated, or, at any rate, the variation of the radiant field tends to become irregular in period, with the result that a slowly cumulative irreversible change gains ground as concomitant, tending to the formation of colourless or coloured products more and more *indifferent* to casual fluctuations of the radiant environment.

This *induration*, which may be regarded as the mode itself by which permanent fast organic pigments are produced in nature, is as yet little understood, but in the case of the fulgides it appears to be analysable into three principal stages.

1ST PERIOD { Chromatropic mutation of fulgide or allo-fulgide } $C_{21}H_{16}O_3$

Suggested structural formula :—

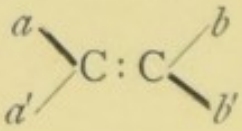


2ND PERIOD { Formation of a structural isomere. Possibly an oxonium-complex, the *oxygen* taking a central position in the complex.

The empirical formula is still $C_{24}H_{16}O_3$.

3RD PERIOD { This structural isomere is meta-stable, readily forming a labile red body, also $C_{24}H_{16}O_3$ which passes to the *photo-anhydride* $C_{24}H_{14}O_2$, which is *labile* in its *nascent state*, stable soon after.[1]

II. *Photo-chemical change and stereo-isomerism.*—Chromatropic phenomena compenetrate insensibly with those leading to the conception of stereo-isomerism. The criteria of this form of isomerism being principally optical, we should expect to find most of the transformations concerned sensitive to light. The use of light not merely as indicator but as effective agent in this branch of physical chemistry is yet in its infancy. We shall only cite here the photo-chemically induced transitions of *cis* and *trans*-isomers in bodies containing an ethylene bond >C=C< with the dis-symmetrical grouping—



in force, the outstanding example of which is that of *maleic* and *fumaric* acids :—

COOH—C—H ‖ COOH—C—H	Maleic acid Γ cis-cis or *cis*-form
COOH—C—H ‖ H—C—COOH	Fumaric acid Γ cis-trans or *trans*-form

The maleinoid form is sometimes termed plane-symmetrical, the fumaroid form axial-symmetric. Its formation from its isomer is accompanied with an evolution of heat.[2] Light

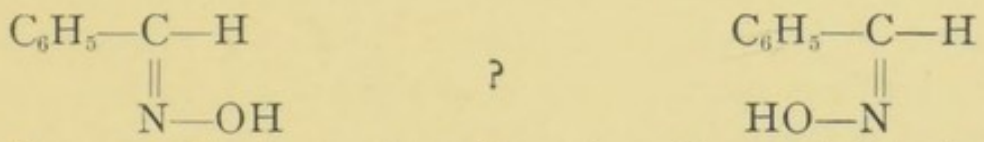
[1] These transitions should be compared with those suggested for the photo-hydrolysis of inorganic salts of the metals, p. 319, where a somewhat similar series of modifications takes place.

[2] On this subject see A. W. Stewart, *Stereochemistry*, this series, p. 156.

generally seems to accelerate the change from the fumaroid to the maleinoid form.[1] Other similar or derivative cases are the conversion of *cis*-cinnamic acid into *trans*-cinnamic acid, with evolution of 35·4 K. of *cis*-furfuro-acrylic acid into the *trans*-acid.[2] All these changes are exo-thermic, and apparently irreversible, though experiments do not seem to have been made on the use of intense ultra-violet radiations, or of plane-polarized infra-red rays in this conjunction.

It is necessary to point out that both forms seem sometimes to be in dynamic equilibrium with a so-called *meso-* or *iso*-acid,[3] and this accentuates the possibility of the reaction, the conversion of the unstable *cis*-form into the stable *trans*-form, being at least potentially reversible.

This form of stereo-isomerism approaches that shown by many carbon-nitrogen compounds,[4] the two extreme forms of the amphimyxis of which are illustrated, in the simplest case, by such an *aldoxime* as—



Benz*syn*-aldoxime. Amphimyxis. Benz*anti*-aldoxime.

Configurations can sometimes be assigned to the *amphi*-body, but it is probable that for such indeterminate intermediary bodies, *static* and *graphic* formulæ are (*vide* p. 179) inappropriate.

That most of the transmutations involved in this region of organic chemistry are affected by light, it may be only catalytically, or actually, effected by light of some kind—due regard being paid to the antagonistic workings of different radiations—may be considered as certain, but exact determinations of the influence of different light-sources are wanting.

[1] Cf. J. M. Eder, *Handbuch d. Phot.*, **4**, 330 (1906).
[2] Liebermann, *Ber.*, **28**, 1443 (1896).
[3] Cf. Stewart, *loc. cit.*, p. 195.
[4] Stewart, *loc. cit.*, p. 197.

In the case of the nearly allied diazo-compounds, in which the group —N = N— is present, several photolytic changes have been studied,[1] but these pertain to a wider rubric than that of stereo-isomeric transmutation.

There remains the vast group of problems centring about an asymmetric multi-valent atom, primarily a carbon atom. It will be remembered that the principal characteristic of these bodies is, that when not externally or internally compensated, they rotate the plane of a polarized light-ray.[2]

Independently of any theory of the interaction of light and matter, we are bound to assume that the rotations measured in these cases are equilibrium-values consequent with a more or less rapid installation of a photo-chemical stationary state (*vide* p. 225), an equilibrium, essentially dynamic in its nature, of balance between the vectors or directed quantities, of the light-ray, and the electro-magnetic field of the molecules responsive to it. That the condition of affairs does not always revert, subsequent to this determination, absolutely to the *status quo ante*,[3] that is, that there is sometimes manifest an imperfect elasticity in the optical rotary power of the molecule in question, corresponding to a permanent photo-chemical deformation—is shown in the phenomena of muta-rotation, and further illustrated in the actual inversion of cane-sugar by ultra-violet light.

A beginning of a completer photo-chemical study of this question has been made in the investigation of the influence of the wave-length of the light on the optical rotary power of the molecule.[4] The parallelism between rotation-dispersion and colour-dispersion is very considerable, and the existence of anomalous rotation dispersion shows that the same photo-chemical equilibration is called into play as in chromatropy,

[1] O. Ruff and V. Stein, *Ber.*, **34**, 1658 (1901).

[2] A. W. Stewart, *Stereochemistry*, this series.

[3] Which virtuality or reversibility of the light-action is the condition of its being a single-valued *physical* property of the substance.

[4] Cf. Chr. Winther, "Polarimetric Researches and the Theory of Optical Rotation," *Zeit. phys. Chem.*, **41**, 161 (1902); **45**, 331 (1903); **60**, 563 (1907); **60**, 685 (1907).

albeit differently manifested. So far, attempts to separate optical antipodes from synthetic compounds potentially but not actually "optically active," by means of circularly polarized light, have not been successful.[1]

[1] Henle and Haakh, *Ber.*, **41**, 4261 (1908); cf. also A. W. Stewart, "Recent Advances in Organic Chemistry," p. 251, 1911 (Longmans).

CHAPTER IX

RADIANT MATTER AND PHOTO-CHEMICAL CHANGE

§ 121. Preliminary.

We have to proceed shortly to the main alternative aspect of the mobile photo-chemical equilibrium, to pass from the consideration of light as a *causal agent* of chemical change to light as an *effect* or resultant of chemical change, *i.e.* paraphrased, of chemical changes as causes of light, perhaps the most fundamentally initiative causes thereof. And this *volte face* may perhaps be rendered less abrupt and inharmonious if we achieve it by way of some consideration of the phenomena of "corpuscular radiations," of photo-electric currents, and the analogy of the chemical activity of the former to that of light. Divers and diverse as are the forces of nature, yet their very undying antagonism convokes an equilibrium of power, that *energy* which we have to postulate as constant in the sum of its forms potential and kinetic. Our prime motors derive their force from a conversion of potential into kinetic energy, and the tax which the ambient medium levies upon each such transaction, the death-duty on the element of potential energy passed over to the kinetic condition, is termed increase of *entropy*. Entropy is to energy like the increasing shadow thrown by a setting sun, but ignorant as we are yet of much of the detail in the matter of the diffusion and dissipation of available potential and macro-kinetic energy (*vis viva* of sensible movements) into unavailable potential and micro-kinetic energy (*vis viva* of insensible movements), we are yet more ignorant as to the inner mechanism of the way in which a concentration of diffused radiant energy is effected in life—the photo-synthesis of food and fuel by vegetative life.

§ 122. Cathode Rays and Phototrophy.

Of the numerous physico-chemical changes producible by cathode rays, *i.e.* by streams of negatively electrified particles (electrons) ejected from the cathode when a high tension current is allowed to discharge between metallic electrodes in exhausted vessels, and also, to some extent, by metallic surfaces exposed to intense radiation and by naturally radio-active bodies, only a few can be mentioned here, to illustrate the continuity of the phenomena of electric radiations with those of light and photolysis. We may consider these physico-chemical effects as due to at least two or three interdependent factors.

(*a*) The independent electron possesses a kinetic energy $\frac{1}{2}mv^2$,[1] in consequence of which it exercises an elastic impulse upon impact on the particles of coherent matter. E. Bose[2] has endeavoured to explain the greater part of the effects of β-rays, considered as streams of electrons moving with velocity approaching that of light, solely as consequences of the elastic shock or impact which they communicate to dense matter. It is questionable if this purely mechanical hypothesis is sufficient, though it must be remembered that under the relatively enormous pressures suddenly generated on the impact of projectiles, many auto-catalyzed reactions, such as take place in an adiabatic envelope in which a exothermic reaction is initiated, thus become possible.

(*b*) Taken at large, electrons are not absolutely homogeneous *inter se*. Only a bundle of the *same generation*, originated with the same initial velocity, and henceforth linked together by the same velocity-gradient, form a homogeneous group or *electrion* as it may be called. There remains a similarity between groups of electrons, however, of different velocity-gradients, so long as these are not incommensurable in magnitude, which results in this, that two groups travelling

[1] The "mass" m of an electron, whatever theory of the relativity of motion and time be adopted, is certainly a function of its velocity, *i.e.* of its speed and direction conjointly. Those interested may study the recent researches on the migrations of electrons in fields of force.

[2] *Zeitschr. f. Elektrochm.*, **10**, 588 (1904).

with *different* velocity-gradients exercise a common shearing-stress on the medium they traverse, and this shearing-stress may be regarded as the mechanical analogue of the field of electro-magnetic or radiant energy due to the free electrions, or groups of electrons with a roving commission.

(*c*) Since cathode and β-rays result from a disturbance of electric neutrality (of an electro-static equilibrium), there recoils in the opposite sense to the path taken by the β-rays an equivalent quantity of positive electricity. If this is reflected, it may travel, quasi-independently, in the same direction as the β-rays. Such are the α-particles from radio-active bodies. If given free space in the inverse sense, we have the so-called canal-strahen observed by Goldstein.

Where cathode rays impinge upon dense matter, they induce, according to its constitution, secondary cathode or β-rays, heterogeneous with the primary rays, and X- or Röntgen rays, also varying in homogeneity and hardness (penetrating power) with the nature of the material excited as well as of that of the exciting beam. According to one hypothesis, X-rays are irregular, incoherent pulses of electro-magnetic vibration in the æther, travelling with the speed of light (Stokes). According to another, they are ultra-violet vibrations of very short wave-length and great group-velocity. And according to yet another, they are corpuscular in nature, consisting of neutral couples of α and β-rays travelling together, as it were, an electric image and its inverse, the phantom of a binary molecule.

Independently, however, of any mathematical and mechanical theory of the nature of these new-comers in the field of physics, this radiant matter constitutes a fourth self-consistent state, its units distinguished by their function *sui generis* as self-moving sources of light, electricity, heat, and mechanical strain in ordinary matter.

Corresponding to the much greater dispersion of the centres of force of substances in the radiant state, it is then and there that the elective or selective affinities of the elements have freest play. And it must be remembered that there is no single metaphor borrowed from historical mechanics which can

unambiguously express the nature of chemical affinity. It is not simply a force of attraction, for it is as much manifest in the movements of repulsion of particles of matter as in their movements of attraction. And it is doubtful if it be measurable truly by the same units as physical energy. It is rather an enduring synergy of forces, each battle-wave of which, if it happen to break, liberates a finite, discontinuous quantity of energy.

It was found by Goldstein[1] that the reactions provoked by cathode rays were very similar to those originated by very short ultra-violet rays. The majority of substances in the focus of a cathode discharge become self-luminous, giving characteristic emission spectra,[2] in particular the salts of the alkalies and rare earths. The salts of the alkalies, at least the halogen salts, acquire a coloration which varies with the metal, the halogen, and the exposure. The halides of potassium, rubidium, etc., become permanently coloured, but not the halides of divalent metals. It appears that a partial reduction takes place, but there has been much debate as to whether a *sub*-halide or a solid solution of free metal in normal halide is produced, it being supposed that on intermission of the energy-flux the halide rapidly re-sets and insulates the free metal. On exposure to air and moisture the coloration disappears. By means of the ultra-microscopic method of "dark ground" illumination, it has been shown that the substance becomes optically inhomogeneous, fine nuclei being dispersed in it, to a depth varying with the intensity of the cathode rays.

Schmidt made the interesting observation that the cathodically coloured KCl and NaCl crystals after *short* exposure gave a considerable alkalinity to water, but that this is not obtained if *longer* exposures are given. There seems to be evident here a solarizing or reversing effect similar to that obtainable in many photo-chemical changes,[3] and which we

[1] *Weid. Ann.*, **11**, 83 (1880).

[2] Sometimes called *cathodo-phosphorescence*; cf. G. Urbain, *Introduction à l'Etude de la Spectroscopie*, p. 145 (1911) (Hermann, Paris).

[3] Cf. the well-known reversal of photographic images.

may regard as probably consequent with the heterogeneity of the rays. It would be the cumulative antagonistic effect of the slower moving, less intense rays restoring the equilibrium disturbed by the more intense radiation.

Silver and mercury halides are also altered by cathode rays. The electric potential of the darkened silver chloride is about the same as that of the photo-chloride, but the chemical composition is equally uncertain. Mercurous chloride, Hg_2Cl_2, turns black, whilst mercuric chloride, $HgCl_2$, is said to be reduced to calomel, Hg_2Cl_2, with emission of light (luminescence), the calomel then darkening. But the quantities changed are so small that quantitative confirmation of the decompositions suggested is lacking. In the case of mercuric chloride, the change might be represented by the scheme

$$2\ominus + 2HgCl_2 \rightarrow Hg_2Cl_2 + \{\overset{+}{Cl}.\overset{-}{Cl} \rightleftharpoons Cl_2\}$$

luminescence due to Budde effect in the freed chlorine

one electron being fixed in the liberated chlorine molecule, one in the calomel molecule, this fixation of electrons[1] being concomitant with the *luminescence* in the one case, the *colour-intensification* in the other.

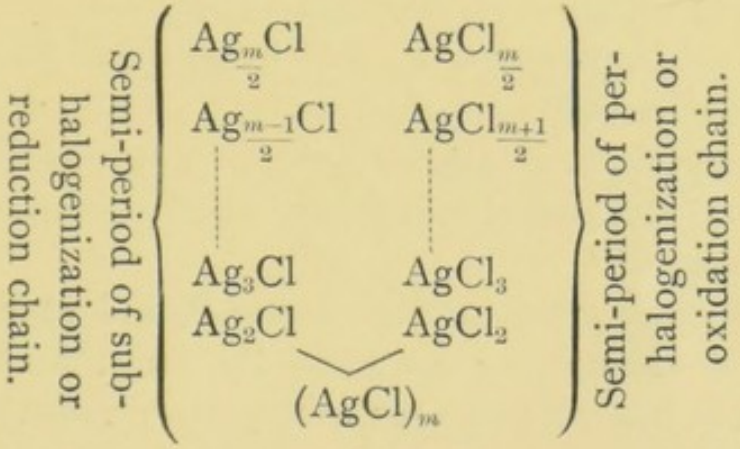
The darkening of dried AgCl, which does not proceed to any appreciable extent *in vacuo* in ordinary light, *i.e.* in the absence of water or other sensitizer, can be effected by cathode rays, though here again in very high vacua the alteration is extremely small. Silver bromide, which is normally yellow, passes to green or greenish-grey, returning to yellow with a better vacuum (a tube yielding harder X-rays) or on heating. In view of the impermanence and ambiguity of the phenomena, Abegg[2] considered that the changes effected

[1] Cf. P. Lenard, *Sitz. ber. Heidel. Akad. d. Wiss.*, 1909, Abh. [3]. pp. 1 *et seq.*

[2] Cf. a review of these actions by H. Herba, *Jahrb. d. Radioactivität*, 4, 307 (1907).

are only physical. It comes to the same thing if we say they are isodynamic, like the chromatropic changes already mentioned. That a valency-displacement is effected is probable, but it may be only virtual, induced as a strain by the shearing stress of heterogeneous radiation, already mentioned as concomitant with the inequality of the velocities of the rays.

We know little of the mode of aggregation of matter in the solid state, but if we suppose, taking the case of *AgCl*, that the formula $(AgCl)_m$ represents a physical, crystallogenic molecular-complex, m being an association-factor, then this group, which *ex hypothesi* reacts as a *unit group* to a light-impulse, may be conceived, under the actinic shearing stress, to undergo a double displacement of its affinity away from the prior condition of equilibrium, the one displacement being in the direction of per-halogenization of a part of the metal (analogous of course to per-oxidation), the other in the direction of sub-halogenization (analogous to reduction), so that we have two opposite chains formed in parallel :—



The sum of all the transformation equivalents on the one side being a positive magnitude, that on the other a negative magnitude, actually equal, the same *multiplicity* m [1] would be fixed for a reversible, *isentropic*, chromatropic variation of the molecule-complex on photo-stimulus, as for the crystallogenesis, the same limit, for the substance in question, determining its

[1] The actual significance of the modulus m would be that of a probability-index, and, in fact, of the cohesion of m identical molecules in one granule.

chromatropy or colour-adaptation in cathode rays, as its mechanical coherence and actual size.

The *strain* thus induced might then either devolve of itself, on cessation of the *stress*, by inner neutralization of the sub- and per-halides engendered, or, in the presence of depolarizers, give rise to irreversible chemical changes. In the scheme suggested, the reduction in one direction is counterbalanced by the oxidation in another parallel to it, so long as the change remains virtual. In consonance with this rather physical than chemical theory, and against the idea of separation of pure metal, Goldstein urges the fact of the cathodic coloration of ammonium halides, and of the halogen compounds of organic amines. The colour obtained is deeper the lower the temperature at which the exposure is made, this seeming to retard the self-damping of the change. But aliphatic halogen bodies also exhibit the coloration in cathode rays. Goldstein inclines to the hypothesis of a "certain virtual rather than absolute separation of acidic and basic, or negative and positive radicles." He expresses the opinion that "through the action of cathode rays, the light-absorption of the *elements* composing a compound is greatly increased. Hence, in an aggregate of elements which is normally slightly coloured, the specific absorption is greatly intensified by exposure to cathode radiation, so that even extremely small quantities become intensely coloured."

In the scheme provisionally suggested, and which supposes two series of *dénouements* set going by the cathode ray, and, so long as not interrupting each other, transpiring through each other for the duration of the coloration, it is evident that segregation of *metal* and of free negative *radicle* are possible extreme consequences which might easily become actual, in the event of depolarizers being present. And it is rare that crystals can be found which do not contain some trace of occluded water, air, or what not. Siedentopf,[1] who made an ultra-microscopic study of cathodically coloured NaCl, and of naturally coloured rock-salt, found that the coloration of crystals of the former usually only extends 0·5 to 1·0μ with

[1] *Physik. Zeitschr.*, 6, 855 (1905).

cathodic radiation, but that induced by radium rays may go in several millimetres. The first after-coloration is due to a microscopic nuclei, which on heating fuse to sub-microns. The particles in the case of NaCl are quasi-crystalline, foliated or spicular. He considers them to be analogous to the gold-particles in ruby glass. The view that a partial reduction of the base to a metallic state is effected is supported by the coloured crystals giving strong photo-electric effects (cf. p. 361).[1]

§ 123. Radio-activity and Photolysis.

The physico-chemical changes produced by radiations from radium and other such bodies pertain to the study of radio-activity, but their affiliation to photo-chemical change is obvious when the characteristic chemical changes produced are surveyed. In the disintegration or radio-active decay of radium, etc., it seems that the seat of intensest activity is the *emanation*.[2] The rays emitted from the emanation as this breaks down are distinguished as—

Emanation.

α-rays.	β-rays.	γ-rays.
Carrying a positive charge, deviable in magnetic field. Rapidly absorbed by most materials. Those from *Ra* have strong photographic action.	Negative carriers, deviable. Identical with cathode rays.	Non-deviable. Equivalent to very penetrating X-rays. Produce secondary radiation in solids, ionization in gases.

Alpha-rays.—According to McClung[3] the ionization-range

[1] Elster and Geitel, *Wied. Ann.*, **59**, 487 (1896). F. Haber obtained violet-coloured KCl in the neighbourhood of the cathode, on electrolysis of the fused chloride.

[2] As the physico-chemistry of radio-active substances is already a profoundly specialized field of work, the brief discussion given here is made entirely in the interest of the side lights thrown by the phenomena and the theory upon photo-chemical changes.

[3] *Phil. Mag.* [VI.], **10**, 163 (1905). [A later value, given by Bragg, *Studies in Radio-activity*, is 7·14 cm. The α-particles have been shown to be atoms of *helium*, which alternate a positively charged with a neutral state.]

in air of the α-rays from radium is about 6·8 cms. Rutherford [1] and Duane [2] state that ionization, photographic action, and excitation of phosphorescence, as well as the induction of secondary radio-activity, by these α-rays stop for the same thickness of absorbing screen, an indication of the close connection of these various phenomena. Rutherford suggests that both the photographic action (or photo-chemical effect) and the excitation of phosphorescence are secondary to "ionization," but it may be objected that the ionization theory is primarily intended to explain the facts of the electric conductivity induced in a medium, whilst photo-chemical change may be brought about without increase in electric conductivity being shown. Such increased conductivity may rather be considered as the anomaly of true photo-chemical equilibration, which is a dynamic adjustment of the inner chemical affinity of the molecule to an outer field of radiant energy.

The α-rays are similar in many respects to the canal-rays found by Goldstein [3] as shot back through a perforated cathode in a vacuum tube, on the side remote from the anode. It was shown by Wien that they consist of particles sometimes positively charged. Schmidt [4] showed that they oxidized a copper plate, but this effect is due to activation of oxygen, as in hydrogen they reduce copper oxide. Later E. Gehrke and O. Reichenhein [5] obtained radiations from the *anode* in vacuum discharge tubes, using fused alkali salts as the anode material. The radiations behaved very similarly in many respects to cathode rays. They give line-spectra which agree closely with those given by salts in a Bunsen flame, but are probably travelling with immensely higher velocity than the positive carriers in such flames.[6] They exhibit, viewed "end-on," pronounced Doppler effects, from which the velocity could be calculated. They are deviable in a magnetic field, and a calculation of the

[1] *Radioactivity*, p. 108.
[2] W. Duane, *C. R.*, **146**, 1088 (1908).
[3] *Wied. Ann.*, **64**, 45 (1898).
[4] *Ann. Phys.*, **9**, 703 (1902).
[5] *Chem. Soc. Trans.*, **95**, 327 (1909).
[6] See p. 397.

mass of the positive carrier, from sodium chloride, based on the anode potential-gradient, the magnetic deviation, and the value $\frac{e}{m} = 9{\cdot}5 \times 10^{-3}$ for the ratio of charge to mass of the hydrogen ion for unit potential-fall, gave the value 21 to 23 times that of hydrogen, *i.e.* a close approximation to the atomic weight of sodium. It is interesting to note that the behaviour of anode rays is very similar to that of cathode rays. J. Stark sees in the α-particles or anode rays of these the originating centres of serial line-spectra ; further, he considers that when their free movement is impeded they bring about chemical change, forming the " latent images " in silver salts, and Weigert's " photo-ferments."

The β-rays from radium and radio-active bodies are identical with cathode rays, which were first obtained outside the focus tube by Lenard, who used aluminium windows transparent to them, and exert the same physico-chemical influences as these. O. Flaschner has recently shown that the β-rays from radium affect the potential-difference of an $\frac{\text{AgBr}}{\text{KBr}}$ solution boundary in the same sense as light does, the sensitiveness being greater the larger the initial potential-difference is made. They also precipitate calomel in an Eder actinometer. β-rays, as already explained, whether obtained from focus tubes or radio-active substances, are heterogeneous, *i.e.* are composed of groups of electrons with different velocity-potentials. They are absorbed according to an exponential law, and the absorption-constant s, calculated from the formula $\frac{\text{E}}{\text{E}_0} = e^{-sd}$, where d is the thickness of the absorbing layer, is a function both of the velocity of the electrons and of the atomic or molecular density of the absorbing substance.

§ 124. Photo-electric Currents.

The absorption of light and radiant energy by gases, liquids, and solids is always accompanied by changes of electric state in these, a fact in harmony with the conception of light

as an electro-magnetic perturbation of the aether, concomitant with a material displacement current. We may classify the effects observed provisionally as follows :—

(*a*) Ionization and consequent increase of conductivity in gases, liquids, and solids directly due to passage of light.

(*b*) Indirect ionization of a gas by reflection or emission of corpuscular rays from a contiguous surface of a denser phase.

(*c*) Concomitant differences of potential and E.M.F.'s developed in a system typified by—

Electrode substance A in *light*.	Conductor / dielectric.	Electrode substance A in *dark*.

the interstitial medium conjoining the electrodes being partially a conductor, partially a di-electric, this latter breaking down to some extent in consequence with the actions scheduled under (*a*) and (*b*) in the foregoing synopsis. In all such phenomena we must remember that any contiguous phase not taken into account immediately, *e.g.* a gas-phase such as air, may play the part of a condenser or extra-capacity, which may sometimes reinforce the effects observed.

§ 125. Photo-ionization of Gases.

Gases are usually poor conductors of electricity. The various ways in which they may be brought to conduct have been very fully studied of late years. The *direct* photolysis of gases is only brought about by radiant energy of great tension and oscillation-frequency. Thus gases may be directly "ionized" by ultra-violet light, by X-rays, and by the γ-rays from radio-active bodies. For the technique and methods of measurement, reference should be made to treatises on the conduction of electricity through gases.[1] The conductivity is

[1] J. J. Thomson, *Conduction of Electricity through Gases*.

attributed to ions or charged carriers which may remain free for some time after incidence of the excitation, but the activity and conducting power of which, in consequence of a recombination, fall off subsequently according to exponential laws. The current does not follow Ohm's law except for a small potential-difference of the measuring E.M.F. in the circuit. A typical arrangement for determining the phenomena with a gas exposed to ionizing radiations is shown in Fig. 43.

This apparatus [1] consists of a brass tube of 5 cms. diameter, the anterior end of which is provided with a fluorspar lens to admit the rays, and the posterior end with a plate

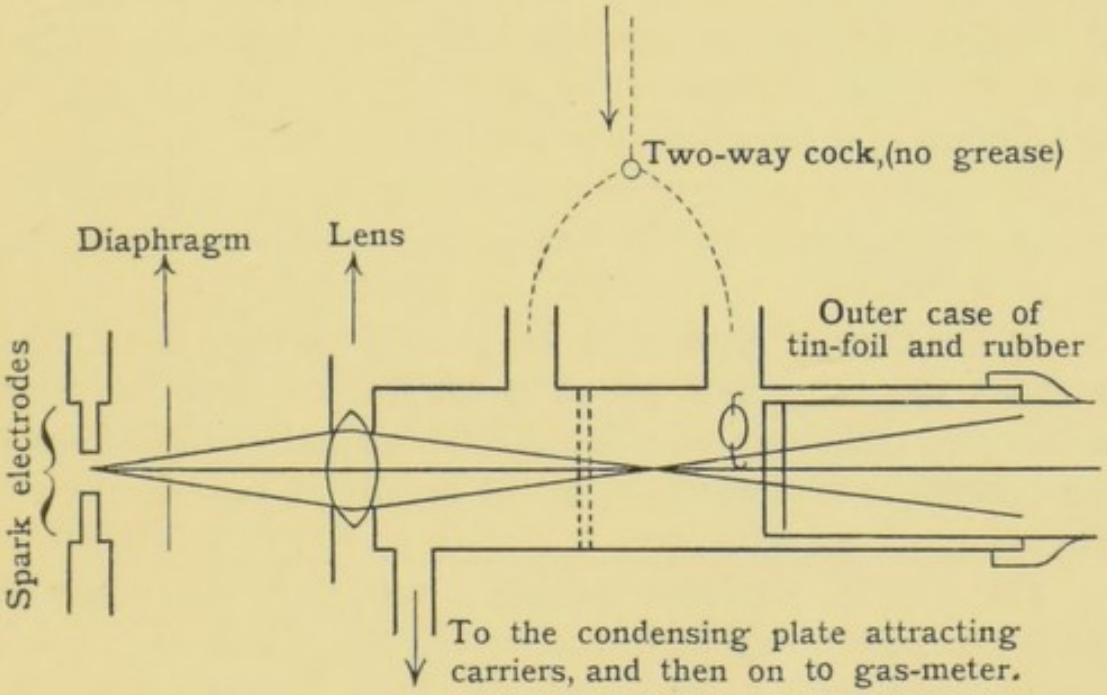


FIG. 43.

of cut quartz-crystal ϕ. The light passes through the space in a concentrated bundle, passing through the transparent quartz-wall without encountering another reflecting mass. The fluorspar lens is of course essential with intense ultra-violet light, but lenses are dispensed with where the radiation is effected by X-rays, etc. The quartz-end could be moved to and fro, so as to alter the thickness of the gas-phase illumined, being fastened on a second tube sliding in the first, whilst the current of gas radiated could be determined by a gasometer in the circuit.

[1] See Lenard's paper.

The actual ionization produced in such cases is determined by the deflections of an electrometer.

The negative ions in gases, whatever their nature, rapidly condense an atmosphere of water-vapour, or of other more easily condensable gases present. The charges carried by the ions produced in air, in oxygen, hydrogen, and carbon-dioxide appear to be the same, and equal to that carried by the H-atom in the electrolysis of aqueous solutions. If, however, the pressure of the gas be greatly diminished, a rapid increase in the ratio $\frac{e}{m}$ of charge to mass is observed.

It appears probable that these ions are components of the photo-ferments already discussed (p. 303), whilst the steady state in ozone formation, for example, is identical with the installation of a saturation current (*vide* p. 256).

The general property of condensing water-vapour may be shown with a steam-jet, which can thus act as a general reagent for such ions.[1]

If the current produced is plotted against the E.M.F. between the condenser plates or electrodes, which serves to attract the positively and negatively charged carriers formed, the general form of curve obtained is similar to that given in Fig. 44.

The current gradually reaches a steady or saturation value for given radiation and increasing E.M.F. between the condenser-plates (which may form part of the ionization-chamber, or the ionized gas may be passed on to a measuring chamber, as shown in Fig. 43). The inversion effect—where the curve changes above the saturation level—occurs when the transverse measuring E.M.F. is sufficient itself to break down insulation and ionize the gas. Its value is directly proportional to the pressure of the gas, being for air at 760 mm. about 30,000 $\frac{\text{volts}}{\text{cm.}}$.

The greater the volume of gas traversed by the ionizing radiation, the greater the absolute value of the saturation current, so that for complete absorption, *i.e.* maximum ioniza-

[1] R. von Helmholz and F. Richarz, *Wied. Ann.*, **40**, 161 (1890).

tion, the current is greater the greater the distance between the electrode-plates of the conductivity-vessel, which is analogous to the increase of conductivity observed in solutions on dilution.[1]

Assuming that equal quantities of positive and negative carriers or ions, q of each are formed per second, each with a charge y, then if a current C is passing, the saturation-current will be $q.y$, q being evidently the degree of ionization. The recombination will take place at a rate proportionate to the

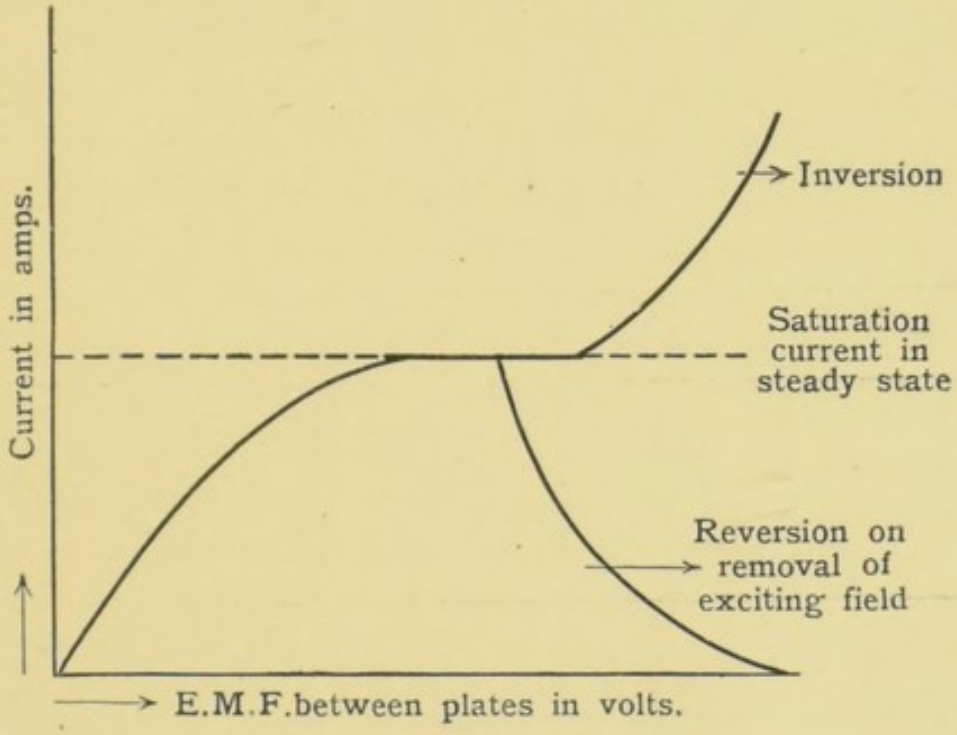


FIG. 44.

instantaneous value of q^2, say n^2, so that for equal proportions of positive and negative ions we have

$$\frac{dn}{dt} = q - \alpha n^2$$

the solution of which, giving the value of n in the steady state, is, if $\frac{q}{\alpha} = k^2$, and since $n = o$ when $t = o$

$$n = k\frac{(e^{2k\alpha t} - 1)}{(e^{2k\alpha t} + 1)}$$

We may note that the arrangement is similar in principal

[1] Cf. R. Lehfeldt, *Electrochemistry*, this series.

and operation to a photo-chemical actinometer, electrical instead of chemical methods being employed to determine the changes produced.

§ 126. Determination of the Mobilities of the Ions, their Coefficients of Diffusion.

The determination of the diffusivities of the ions in C.G.S. units is a difficult problem as they are strongly adsorbed to the walls of the vessels. The following values obtained for *dry* gases are given to indicate the order of magnitude.

Table XXVII.

U = diffusivity for + ion; V for negative; D is the mean value; and $R = \frac{V}{U}$.

Gas.	U.	V.	D.	R.
Air . .	0·028	0·043	0·035	1·54
Oxygen .	0·025	0·040	0·032	1·58
CO_2 . .	0·023	0·026	0·025	1·13
H_2 . . .	0·123	0·190	0·156	1·54

Owing to the greater mobility of the negative ion, differences of potential are readily set up in dry gases, which easily acquire positive charge.

§ 127. Nature of the Ions.[1]

The negative ions readily condense water-vapour, which diminishes their mobility, so that in moist gases the value of $\frac{V}{U}$ approaches unity, and the conditions are approximating to those in liquid solutions. As the values for the same gas are identical, whether the ionization be produced by ultra-violet light, X-rays, or point-discharge, we may assume that chemically the ions are the same.

[1] Cf. J. J. Thomson, *loc. cit.*, and P. Lenard and C. Ramsauer on electricity-carriers in gases, *Sitz. ber. Heidel. Akad. d. Wiss.* Abh. (**32**), 1910.

Lenard and Wolff[1] showed that gases ionized indirectly by light acting on zinc or a fluorescent substance also condense water-vapour, as does ultra-violet light filtered through quartz. Richarz[2] showed that X-rays had the same effect. The question whether "dust-nuclei" are pre-existent in such cases, or forced into being by the ionizing rays has been much debated. The condensation-nuclei in gases may be compared in some respects with the coagula of colloids produced electrolytically.[3]

§ 128. Photo-electric Effects with Condensed Phases.

Hallwachs, following Herz, found in 1888 that a negatively charged surface loses its charge upon illumination, the adjacent gas-phase becoming a unipolar conductor. It is necessary that light be absorbed, but on the other hand all such absorption of light is not accompanied by the photo-electric effect in the adjacent gas-phase. Subsequent researches have shown that an uncharged surface takes a positive charge when exposed to light; the effect, measured as a current in the gas-phase, depends very much upon the nature and condition of the surface. Thus a surface wetted or coated with a soap-film does not react nor discharge in light. Although the effect is very general, it is most marked and most easily studied with metals, metallic sulphides and halides, and organic dye-stuffs. Generally the effect diminishes in intensity as the wave-length of the incident radiation is increased, but may extend into the visible spectrum, depending upon the intensity of light and atomic or molecular volume of the substance.

Brightly polished metals give the strongest effects of this kind, the sensitiveness increasing the more electro-positive the metal, *i.e.* with its solution tension, on Nernst's theory. It is possible that the effect is often complicated by the presence of

[1] *Wied. Ann.*, **47**, 443 (1899).

[2] *Wied. Ann.*, **59**, 592 (1896). On condensation of nuclei and ionization consequent upon chemical reactions, see A. Uhrig, *Inaug. Dissertat*, Marburg, 1903.

[3] On the coagulation of proteins by ultra-violet light, cf. G. Dreyer and O. Hansen, *C. R.*, **145**, 234 (1907). [On pre-existence of dust-nuclei' see Lenard and Ramsauer, *Heid. Akad. sitz. ber.*, V. p. 46.]

adsorbed or condensed layers of gases such as oxygen, removal of which facilitates a discharge or emission of rays by the metal similar to rays or negative corpuscles. Wulff[1] has shown that the photo-electric effect with platinum could be increased tenfold by electrolytically charging the surface with hydrogen. Closely connected with the polarization of the surface by oxidizing gases are the phenomenon of passivification and photo-electric fatigue.

The alkali metals in vacuo are extremely sensitive in this phenomenon, giving effects for the rays of the visible spectrum. The following table shows the colour-sensitiveness of three alkali metals, according to Elster and Geitel.

TABLE XXVIII.

Light.	Na.	K.	Rb.
Blue	7·8	30·0	87
Yellow . . .	8·2	3·5	340
Orange . . .	3·1	2·2	182
Red	0·2	0·1	21
White	22·0	53·0	540

The numbers indicate the sensitiveness.

Amongst the more sensitive solids are fluorspar, sulphides (not sulphates) of metals, many metalloids and hydroxides in a dry state, and dried halides of silver and lead. Solutions and solid specimens of most organic dye-stuffs also, and of most substances with strong selective absorptions, unite in giving this effect.[2] Since, however, the phenomenon depends decisively upon the gas-phase also present, quantitative data are only of value when the nature and condition of this are also accurately specified.

The form of the curve for the current in the ionized gas-phase is similar to that for the case of direct ionization, and the corpuscular radiation emitted can bring about condensation of vapours.

[1] *Ann. Phys.*, **52**, 433 (1894).

[2] See O. Knoblauch, *Zeit. phys. Chem.*, **29**, 527 (1889); and G. C. Schmidt, *Wied. Ann.*, **64**, 708 (1898).

In each photo-electric effect we have then really to consider the changes in a triple aspect: (*a*) change within the gas-phase, (*b*) change in the interfacial layer between gas and solid, (*c*) change within the solid phase. In a large measure, the effect is a "skin-effect," the interfacial layer referred to in (*b*) being the actual focal plane of maximum importance, an aspect of the problem not unconnected with the universal importance of surface-dynamics in chemistry, and further with the occurrence of many of the most powerful and energetic therapeutic or physiologically important substances in the epidermal layers of plants.[1]

The results of this skin-deep battlefield must be looked for both in the gas-phase and the contiguous solid phase. The skin behaves as an electric double layer,[2] a definite difference of potential being maintained across it. The emission of negative electricity—or electrons—by the solid does not depend only upon this and the light, but also upon the gas-phase, so that the precise determination of the electrionic emission-function of a given solid is a matter of considerable difficulty, since it is measured by the ionization in the gas. Varley[3] found that the emission was initially less the greater the pressure of the gas, for one and the same gas, whilst it was greater in hydrogen than in air. Lenard[4] found further that in very high vacua an illuminated surface continues to discharge negative electrons even when there is a small surface positive charge, that is, the tension is capable of overcoming a small polarization. In general there appears to occur a kind of induction, corresponding in part to the preliminary work of ionizing the gas.

[1] For further researches on the photo-electric effects in, comparatively speaking, anhydrous systems, see Stoletow, *C. R.*, 108, 241 (1889); Elster and Geitel, *Wien. Ber.*, 101, 703 (1892); *Wied. Ann.*, 48, 625 (1893); E. von Schweidler, *Phys. Zeit.*, 4, 136 (1902); *Wien. Ber.* (2), A., 113, 1120 (1904); W. M. Varley, *Phil. Trans.*, 202, 439 (1903).

[2] H. von Helmholz, *Wied. Ann.*, 7, 337 (1879).

[3] *Phil. Trans.*, **302**, 439 (1904).

[4] P. Lenard, *Ann. Phys.*, **8**, 149 (1902).

§ 129. The Electronic or Corpuscular Theory of the Effect.

According to the electron theory, the photo-electric effect is due to the expulsion from the metal, or other reacting surface, of unit electric quantities, which ionize the electrically neutral molecules of the gas-phase adjacent. This theory has proved of great value in correlating the phenomena mathematically. The simplest condition is when the discharge is effected in a very high vacuum, in which case direct comparison of the emissivities of different metals is facilitated whilst the influence of the wave-length and polarization of the exciting light can also be more easily determined. The quantitative interpretation of the phenomena can then be attempted, in terms of the following variables:—

N = number of corpuscles emitted per unit area per second
e = charge per corpuscle
m = mass of corpuscle
v_0 = initial velocity of corpuscle

When the surface is illuminated *in vacuo*, the movements of the particles are determined by the electric and magnetic forces of the field, the electric gradient accelerating their motion, the magnetic field deviating the lines of movement. The values obtained for the ratio e/m under these conditions are comparable with those calculated for cathode and β-rays.[1] The initial velocities vary both with the nature of the surface and the wave-length of the exciting rays.[2]

§ 130. The Influence of Wave-length.

It was found by E. Ladenburg[3] for platinum and copper that the initial velocity is directly proportional to the oscillation frequency of the incident light, when short ultra-violet light is

[1] Cf. J. J. Thomson, *Conduction of Electricity through Gases*, p. 250.
[2] *Ibid.*, p. 268.
[3] *Phys. Chem. Centrbl.*, **5**, 225 (1908).

employed. The following table shows the results obtained for copper.

TABLE XXIX.

λ	n	a	$\frac{n}{\sqrt{a}} = v_0$
274 $\mu\mu$	1·095	35·0	1·85
260 ,,	1·15	38·5	1·855
247 ,,	1·21	42·0	1·865
242 ,,	1·24	—	—
237 ,,	1·265	46·0	1·863
229 ,,	1·31	50·5	1·84
220 ,,	1·35	54·0	1·83
218 ,,	1·375	—	—
215 ,,	1·39	57·5	1·835
210 ,,	1·43	59·0	1·86
204 ,,	1·47	62·0	1·87
201 ,,	1·49	64·0	1·86

Here λ = wave-length
n = relative frequency
a = galvanometer deflection
v_0 = initial velocity.

P. Lenard has also shown[1] that the initial velocity does not depend upon the intensity of the light, as ordinarily expressed, but rather upon the quality, whereas the *number* of corpuscles emitted depends upon the intensity. There appear to intervene here considerations similar to those effecting the deviations from the Bunsen-Roscoe reciprocity law of photographic practice.

It has been suggested by J. J. Thomson that the action of light in the case of this photo-electric effect is comparable with that of a detonator, or that the light-ray serves only as it were to release a trigger, the energy of the ejected electron depending purely upon the nature of the atom it was released from, that is, the action consists essentially in an acceleration

[1] This result has been recently contradicted by Hughes. He asserts that the *energy* is proportional to the frequency, not the velocity, see *Phil. Trans.*, A. **490**, p. 216 *et seq.* (1912).

of a spontaneous atomic disintegration.[1] Against this view is to be set the intimate dependence of the initial velocity upon the oscillation frequency of the light. The process does not occur with the casuality and incommensurability of cause to effect such as obtains on laying a spark to a powder-mine, but the emission is syntonized or tuned to the exciting rays.

Recent experiments by Thomson and others show that clean surfaces of the alkali metals *in vacuo* are continually emitting electrons even in darkness. But it would probably be difficult to prove in this case that the field was clear of all vibrations which might provoke emission of the corpuscles. A distinction has been drawn by Lenard between the "outer" and "inner" velocity of the electrons. The latter refers to their movement in orbits confined to the solid phase, the former to their escape into the gas-phase. A certain acceleration of the electrons in the surface layer would be quite possible, without the inner velocity becoming great enough for complete expulsion.

§ 131. Order of Sensitiveness of the Metals.

As already stated, this agrees on the whole with that order of rank of the metals according to their contact-differences of potentials, though with some noteworthy anomalies, particularly in the cases of Mn, Fe, Cr, Au, Ni, and Ce, all metals which exhibit the phenomena of chemical and electric passivication.[2] The same order of rank, within a little, is obtained for the photo-echnic action of metals, that is, their capacity for fogging a photographic plate when left in contact with it.

[1] The hypothesis of atomic disintegration in explanation of this effect has also been advanced by Sir William Ramsay and H. Spencer and by G. Le Bon (*L'Évolution de la Matière*).

[2] See p. 237.

§ 132. Photo-electric Fatigue.

The emissivity of a clean metallic surface exposed to ultra-violet light diminished after a certain amount of exposure.[1] This fatigue varies very much with the metal, the light, and the gas-phase present. Although polarization by superficial oxidation, or by an adsorbed layer of oxygen seems a plausible explanation, it must be noticed that the fatigue has also been obtained for metals exposed in very high vacua. Yet the metals exhibiting it most pronouncedly (Au, Ag, Pt, etc.) are just the ones likely to contain dissolved, occluded or alloyed gases, whilst the liquid alloy of K and Na, and the metal Rb, which are much less liable to the fatigue, have little tendency to dissolve gases. The fatigue may continue to increase in the dark after cessation of the exposure.

Whilst Ramsay and Spencer concluded that the "tiring" or fatigue-curves of the photo-electric effect with zinc showed breaks or discontinuities, H. Allen[2] finds that his results are well represented by an exponential function of two terms. Pocchettino,[3] who has investigated the photo-electric effect with anthracene, finds a similar fatigue, the surface becoming positively charged. This may be concomitant with a polymerization to di-anthracene, although it is uncertain what catalytic effect traces of gases may exercise. The secondary decay of the positive charge follows a similar exponential function for that holding for amalgamated zinc.

It is desirable to note here that the fatigue may be revived by heat, so that the same antagonistic action of radiations of different period appears to obtain for this effect also.[4]

Ramsay and Spencer suggest that the phenomena of fatigue with elements like zinc, corresponding as they do to a virtual ennobling of the metal, point to something of the

[1] Cf. Stoletow, *C. R.*, 108 (1889).

[2] *Proc. Roy. Soc.*, **78a**, 490 (1907).

[3] *Atti R. Accad. Lincei Rom.* [5], **15**, 171 (1906).

[4] For an electro-chemical interpretation of Luther and Weigert's results with anthracene in light, see A. Byk, *Zeit. phys. Chem.*, **62**, 454 (1908).

nature of transmutation of the elements. Certain it is that the phenomena are similar in character to the well-known induction of a passive state in certain metals, either brought about in electrolysis, or by treatment with substances of high oxidation-potential, such as concentrated nitric acid. This resemblance is probably actually based on an identity of the process obtaining. Although the fatigue, photo-electrically, and the chemical passivification of metals, are generally ascribed to activated oxygen, it is not impossible that nitrogen also plays a part, and that in the following manner. Considered electrically as a process essentially transacted in the electrical double layer at the surface, one feature of the phenomenon corresponds to the charging of a condenser by an electro-magnetic field of very high frequency. There will necessarily be a concentration of the current contiguous to the surface of the metallic conductor, analogous to the well-known "throttling" of the current when a wire is traversed by an alternating current, which would correspond to the fatigue in light. In this polarization, it is quite possible that chemical union of the elements of nitric acid may be effected, as is in fact brought about on a larger scale. If the measuring E.M.F. is not strong enough to maintain depolarization, the concentrated nitric acid may persist long enough to passify the metal. This does not of course explain the latter effect, but brings the two into one issue. The facts and theories on the passivification—or passifying—of metals by nitric acid, etc., or by anodic polarization in electrolytes, have been comprehensively reviewed by Fredenhagen.[1] As an objection to the theory of a superficial oxidation, Fredenhagen points out that the passive metal does not behave differently as regards polarization of light by reflection. But not only does this point require more careful experiment, taking the colour-range of the light into account as well, but it may be pointed out that a fresh surface of a metal exposed to light is necessarily immediately slightly polarized, electro-chemically speaking, or solarized, photo-chemically speaking, so that considerable subtlety would be necessary to devise a crucial test,

[1] *Zeit. phys. Chem.*, **6**, 30 (1908).

since the light used as indicator of the state of the metal surface, in respect of its own state of polarization, is itself an effective agent in altering the state of that surface. But no doubt by maintaining a constant beam of monochromatic, definitely polarized light, and subjecting a movable metal surface to it, which could be independently passified and activated, definite conclusions could be reached as to the relation of the electro-chemical state of the surface to the optical properties of the reflected beam. It is well known that light undergoes a phase-change at the surface of metallic reflectors which is no doubt intimately related to the photo-chemical adjustment taking place concomitantly.[1] In this connection we must note the important fact discovered by Elster and Geitel of the influence of the orientation of the beam upon the magnitude of the photo-electric effect. Using the liquid alloy of potassium and sodium,[2] these workers found that for plane-polarized light the emission is greatest when the light is polarized at right angles to the plane of incidence, that is, when the electric vector of the beam is normal to the surface. If a be the angle between the planes of the electric vector and the plane of incidence, then the current for non-polarized light is given by the equation

$$C = A \cos^2 a + B \sin^2 a$$

expressing the actions of both the perpendicular and planar components. The emission of a type of secondary cathode rays by metals exposed to Röntgen rays has been studied by J. Laub,[3] the phenomenon is evidently closely connected with the ordinary photo-electric effect. He finds (*a*) that the emission is stronger the greater the density of the substance, (*b*) the

[1] Owing to the complication of the process by irradiation and dissipation of energy, and by diffusion of the reacting molecules out of the immediate zone of change, the effect is bound to be affected by hysteresis. The incidence of a hysteresis in the phenomenon of electrolytic activation and passivification has been studied by Salmon, *Zeit. phys. Chem.*, **24**, 54 (1897), by Cottrel, *ibid.*, **42**, 395 (1902), and especially by Luther and Brislee, *ibid.*, **45**, 216 (1903).

[2] *Wied. Ann.*, **5**, 433 (1894); **61**, 445 (1897).

[3] *Ann. Phys.* [4], **26**, 712 (1908).

number of corpuscles emitted varies with the intensity of the Röntgen rays, (*c*) the initial velocity of the corpuscles depends upon the hardness of the rays, (*d*) the effect is only slightly dependent upon the polish, but is greater for grazing incidence of the beam.

§ 133. Photo-electric Cells and Currents.

The phenomena now to be described differ principally from those just dealt with in the presence of a sensible amount of a liquid phase, and, indeed, in the presence of aqueous solutions. The variety of photo-galvanic combinations is considerable,[1] and the analysis of the effects, particularly in regard to the localization of the actual seat of the effect, far from complete.

We may provisionally divide the problem into two parts: (i.) the change of conductivity of solid, especially photo-sensitive salts and metalloids exposed to light; (ii.) the installation of permanent potential-differences and effective electromotive forces by light acting on suitable combinations.

§ 134. (I.) Conductivity Changes.

The field of this research is nearly coincident with that just dealt with, the substances exhibiting a change of conductivity in light being very numerous. The case of selenium and other such elements has already been considered (p. 234). On the corpuscular theory, increased conductivity means increase either in the numbers or mobilities of free electrons. In the case of binary compounds, the behaviour of the silver halides is typical and has been most thoroughly studied, and of these silver iodide shows the greatest range of phenomena.

It was discovered by Arrhenius[2] that silver halides exposed to light became much better conductors of electricity, the maximum effect being shown in the same region of the spectrum for which the absorption and photo-chemical activity

[1] See footnote, p. 383.

[2] *Sitz. ber. Wien. Akad.*, 1887, p. 97.

was greatest, whilst optical sensitizers such as dye-stuffs conferred a second maximum upon them. He considered that the increase of conductivity was due to a dissociation of the halide into ions.

Scholl[1] has made a very comprehensive study of the behaviour of silver iodide. He found that atmospheric oxygen played an important part in the phenomenon, undergoing a photolytically induced transvection through the dissociated iodide and simultaneously regenerating the halide. Hence a silver iodide film does not darken much in light in the presence of oxygen, but becomes turbid. Iodine vapour can play a similar *rôle,* the net result being a movement of iodine through the layer of halide in the direction of the beam of light. Scholl prepared films of solid silver iodide by continued anodic polarization of sheet silver in potassium iodide saturated with silver iodide. These films were about 1 to 10 μ thick, and translucent. They were placed in solutions of potassium iodide and exposed to light. The difference of potential, due to exposure to light, between the solid phase and the solution next to the film was found to be of the order 1/30 volt. With regard to the increase of conductivity, Scholl concludes—

(*a*) That new ions are produced, but that the negative ion is not the ordinary iodion, I′, in electrolysis, its mass, as calculated from Nernst's diffusion-theory, being of the order of electronic masses. In violet light silver iodide becomes metallically conductive, but shows no emission of corpuscles, whereas in ultra-violet light there is considerable emission and only slight increase of the internal conductivity.

(*b*) Whilst originally, as first prepared, only sensitive about $\lambda = 430\ \mu\mu$, the illumination actually sensitizes the halide for the longer wave-lengths.

The photo-iodide formed and the correlative sensitiveness decays in the dark and on illumination by red light,—it is unstable out of the light it is formed in, and reverts to ordinary yellow iodide.

[1] *Wied. Ann.*, **68**, 145 (1889).

§ 135. (II.) Photo-electric Potentials and E.M.F.'s.

The practical study of photo-electric combination was first made by E. Becquerel.[1] It is obvious that whatever we understand by positive electrification, this will be taking place in the opposite sense to that of the emission of negative quantities, that is, in this case, in the interior of the film, and if the positive carriers are very active, is equivalent to the formation of anode rays of greater or less penetrating power, moving in the direction of the incident light. Becquerel made use of identical plates of silver coated with halide, and immersed in dilute H_2SO_4 as electrolyte. On exposing one electrode to light, keeping the other in darkness, a measurable current could be obtained, so that the combination could be used as an actinometer. The use of H_2SO_4 complicates the system unnecessarily, and makes it liable to secondary polarizations reducing its reliability. But Becquerel showed that while the ordinary halide had only a maximum of reaction in the blue-violet, exposure to this made it less sensitive to longer wave-lengths on subsequent illumination by these. He considered that there was a liberation of halogen effected which conferred an oxidation-potential on the illuminated electrode. Other researches on these cells were made by Rigollet, Hankel, Minchin [2] and others, but the most important work is due to Luggin, Wilderman, and Goldmann. H. Luggin investigated the conditions of formation of photo-electric cells both by the deflection method and by a compensation or null method.

Regarding the compensation method. Suppose that in order to keep the potential of an electrode constant in the dark it requires a current of potential P, in light a current $B + p$, then p is the measure of the photo-current. The sign of the current is fixed by convention with respect to a standard combination such as the mercury-calomel one. If the potential of this be taken as zero, a positive current is one charging the

[1] *La Lumière*, **2**, p. 121.

[2] Cf. *Jahrb. d. Radio-aktiv.*, **2**, 186 (1905).

blank metal. For moderate intensities of light Luggin found that the current was given by

$$V_0 - V = pb \quad \text{where } b = \frac{dV}{dp}$$

i.e. V, the light-potential, by the equation

$$V = V_0 + p\frac{dV}{dp};\ b = \frac{dV}{dp}$$

The following table shows the values observed and calculated from this formula with a platinum electrode coated with silver bromide. The light-strength was 19·7 Hefner-meters.

TABLE XXX.

Photo-current per cm.² in amps. × 10⁻⁸.	V observed.	V calculated.
+ 0·0362	+ 0·2675	+ 0·2582
+ 0·243	+ 0·2313	+ 0·2303
+ 0·0786	+ 0·1515	+ 0·1566
+ 1·587	+ 0·0406	+ 0·0481
+ 2·272	− 0·0544	− 0·0447
+ 3·149	− 0·1527	− 0·1644

$$V = 0{\cdot}263 \text{ volts};\ b = 1355\ \frac{\text{volts cm.}^2}{\text{amps.}}$$

Luggin remarks that both V and b show variations according to the value of the initial polarization V_0, and hystereses depending upon the history of the electrode, *i.e.* prior illumination. Further, with great intensities of light the p, V curves are no longer straight, but become convex from the origin, cutting the V axis at an acute angle. The value of V for this intersection, when $p = 0$, Luggin terms the *equilibrium-potential*, and it corresponds, electrically, to a self-polarization of the reacting system, or, as Luggin points out, to what is termed photo-chemically, *solarization*. That is, to the adjustment of a neutral stasis or indifference. As any increase of the depolarizing subsidiary current lessens this tendency to self-polarization (in the same manner that chemical sensitizers act) the phenomenon is best studied by following galvanometer

deflections. Luggin regards it as due to an induced oxidation-process, opposite in sense to the photolysis, and tending to reduce the spread of this.

We may note in passing that the equation for the induction of the current

$$V = V_0 + p\frac{dV}{dp}$$

is analogous to the Gibbs-Helmholz equation for the E.M.F. given by a (thermo)-chemical change

$$Q = H + T\frac{dQ}{dT}$$

where Q is the potential, H the heat of the reaction, and $\frac{dQ}{dT}$ the temperature-coefficient.

Luggin concluded that "the strength of the current which an illuminated electrode such as Ag | AgCl gives on illumination is, taken independent of its direction, a measure of the work done by the light."

Goldmann[1] has extended Luggin's work, using solutions of dye-stuffs as the medium. He first tested the statement of Nichols and Meritt[2] that such solutions show an increase of conductivity when exposed to light. He finds that this is only true for the solution immediately adjacent to an electrode simultaneously exposed, that is, when a depolarizer is present, allowing the formation of a current. He investigated the conditions of this current, using semi-transparent electrodes of thin films of metal deposited on glass. The dye-stuffs employed were eosin, uranin, fluoresceïn, cyanin, and rhodamin, and similar results to those of Luggin and Scholl were obtained. We have two series of results, according as—

(*a*) There is no extrinsic E.M.F. inserted in the circuit, but the current is measured by the deflections of an ammeter. The potential differences may be determined by a quadrant electrometer or a Lippman capillary electrometer.

(*b*) The electrode potential is controlled by an applied E.M.F., which may be arranged to compensate the light-effect.

[1] *Ann. Phys.*, **27**, 449 (1908).
[2] *Phys. Rev.*, **19**, 415 (1904).

The more important of Goldmann's results are as follows :—

The actual zone of change is a capillary layer at the electrode of about 1 to 10 μ thick.

Using the arrangement described in (*a*), the strength of the current increases with the concentration of the dye-solution, as may be seen from the following numbers :—

i = current	100	70	35	10	5	2	0	0
Concentration	1	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{1}{16}$	$\frac{1}{32}$	$\frac{1}{64}$	$\frac{1}{128}$

The photo-current (or photo-lysis) is directly proportional to the superficial area exposed, and, within certain limits, to the light-strength. It is nearly independent of the outer resistance of the circuit. This condition points to the limitation of the action to a capillary-layer, and militates against the opinion sometimes expressed that what is measured is the potential-difference between an exposed and the unexposed electrodes. Similar curves are obtained for the growth of the current with time as were found by Luggin, the current value increasing less rapidly with time, and falling off gradually upon cessation of exposure. The results accord with Scholl's deduction that negative electrons are expelled into the solution, whilst positive carriers move to the metallic electrode, which therefore becomes anodically polarized. The current usually flows from the non-exposed to the exposed electrode.

(*a*) As with the anhydrous combinations previously considered (ordinary photo-electric effects), it is found that the maximum charge or potential-difference effected does not depend upon the intensity of the light, which affects the average current, but does not determine the voltage, which is primarily a function of the quality of the light absorbed.

(*b*) The passage of positive carriers into the electrode, or the anode-ray formation, progresses till a stationary state is reached, when the charging by light and the losses by side-conduction, etc., counterbalance each other. In a closed circuit a definite current is installed, but Goldmann states that the maximum value of the E.M.F. is not a steady one.

(*c*) In agreement with the principle of least action, the

exposure develops a counter E.M.F., tending to oppose the direct action of the light.

The actual process of charging may be approximately represented as follows. Assuming that the capacity (polarization-capacity) of the electrode is a constant and limited quantity, the velocity of increase of the potential-difference effected is a measure of the excess of the rate of charging over loss or dissipation of the charges, by recombination of ions, etc. Hence we have

$$\frac{dV}{dt} = \frac{1}{G} \cdot (q - aV),$$

as follows from the general expression $V = \frac{\phi}{G}$ where $\frac{dV}{dt}$ is the rate of increase of potential, G the capacity of the electrode, q the charge effected per unit time, and a a proportionately constant, the term aV representing the rate of decay of the charge. This expression is identical with that of Luggin (p. 373)

$$\frac{dV}{dt} = V_0 - pb$$

if we write for $V_0 = \frac{q}{G}$, and put $pb = -\frac{a}{G} \cdot \frac{dV}{dp}$.

This, however, only gives the law for an early period, when the rate of change is a simple function of the light-strength. To obtain an expression for the process in the neighbourhood of the first neutral state, then when the charging is just balanced by loss, the decay-term must be analyzed into factors. It may be regarded as summed of a loss independent of the light (decay in dark), and a loss actually induced by light (consequent with the heterogeneity of the light, radiations of different quality coming more pronouncedly into working as the time of exposure is prolonged). Calling the discharge-factor in darkness q_D, the discharge-factor in light q_L, these being regarded as independent, we get for the rate of change in light

$$\frac{dV_L}{dt} = \frac{q - (q_L - q_D)V}{G}$$

and

$$-\frac{dV_D}{dt} = \frac{q_D}{G} = f_2(V)$$

for the velocity of decay in the dark. If both $\frac{dV_L}{dt}$ and $-\frac{dV_D}{dt}$ are plotted against V, straight lines are obtained, inclined to the axis V, superposition of which gives the light-effect proper. The extrapolated value obtained by prolongation of the curve gives the maximum charge effected, which Goldmann terms the *photo-electric potential.* It is independent of the intensity of the light, but dependent upon its quality; that is, on the corpuscular theory, it measures the initial velocity of the electrons. The strength of the field near the electrode increases to a limit depending upon G, the polarization-capacity of the electrode. As the equilibrium consequent with polarization approaches, the number of free charges, q, released per unit time, diminishes.

The Decay of the Induced Current.

Goldmann observed that the decay or decline of the photo-current, when the light was cut off, did not follow a simple exponential function, but exhibited an actual *recoil*, the potential becoming positive after passing through the zero value. The positive charge effected then decays slowly with time. Hence there appears a considerable analogy between the process and the charging of a condenser, the discharge of which is well known to become oscillatory under certain conditions.

§ 136. The Photo-current $i\left(\frac{dV}{dt}\right)$ in the Stationary Condition.

To estimate this, Goldmann plots the ampères measured by the galvanometer against the corresponding values of the potential-difference determined electrometrically. It is found that the magnitude of the steady current is not proportional to the light intensity, but relatively more considerable for lower intensities than higher. That is to say, the efficiency

or transformation-equivalent of light into electric energy diminishes in this case for high intensities.[1]

This decline of the efficiency with high intensities is attributed to the anodic polarization already referred to. It follows that for actinometric purposes direct proportionality between $i_{stat.}$, the measure of the steady current, and light-intensity, is most favoured, and the range of its validity widest when the E.M.F. of polarization is a minimum. Hence both the external resistance and the polarization should be kept small. Assuming that R, this external resistance, is constant, the value of the current i may be found as follows. The charge given to the electrode is

$$\int_0^t (q - i)dt$$

which effects an E.M.F. equal to the potential-gradient in the circuit, *i.e.*,

$$\frac{1}{G}\int_0^t (q - i)dt = iR$$

hence

$$\frac{di}{dt} = \frac{1}{GR}(q - i)$$

and

$$i = q\left(1 - e^{-\frac{t}{RG}}\right) = q\left(1 - e^{-\frac{t}{\theta}}\right)$$

Goldmann found this exponential equation fairly representative, but noted that the actual curves of growth of the effect appeared to be compounded of two effects superposed, an initial instantaneous action which is rapidly adjusted, followed by a slower change, the adjustment of which is expressed by the equation just given. Inversely, a similar duality is noted in the decay-process. We shall see shortly that a precisely similar phenomenon holds for the phosphorescence in alkaline earth phosphors.

[1] A similar conclusion is reached as to the efficiencies of several photo-chemical reactions.

TABLE XXXI.

E.M.F. of cell with non-polarizable electrodes; compensated circuit resistance *ca.* 3×10^5 ohms.; Pt. film electrode in *rhodamin* illuminated by projection. Nernst lamp values of i_L from $i_L = 40 + 270(1 - 10^{-0.1413t})$; here $i_x = 40$ is the "initial expansion" value just referred to. The decay values of i_D are obtained from the similar equation—

$$i_D = 45 + 217{\cdot}6 \times 10^{-0.1037t}$$

t is in minutes, i in $4{\cdot}10^{-10}$ ampères.

t	i_L obs.	i_L calc.	t	i_D obs.	i_D calc.
¼	43·5	(61·0)	¼	273·0	(249·0)
¾	97·0	(98·5)	¾	237·0	(227·0)
1	115·0	115·0	1	222·5	(216·4)
2	169·5	169·0	2	180·0	180·0
3	207·5	208·0	3	150·5	151·3
4	234·5	236·5	4	129·0	128·7
5	256·0	257·0	5	111·0	111·0
7	282·3	282·3	7	84·7	85·9
9	296·5	295·5	9	71·0	70·4
10	302·0	299·8	10	65·0	65·0
			12	58·3	57·4

The decay curve in darkness is similarly best represented by a sum of two exponential terms of the type $i_t = i_0 \cdot e^{-\frac{t}{\theta}}$ with different time-constants.

Arrangement as in (b); *Control—E.M.F. inserted.*— Goldmann found, with Luggin and other observers, that on introducing an independent E.M.F. into the circuit, cathodic polarization of the photo-electrode increased the photo-current, whilst anodic polarization diminished it, acting like Luggin's solarization current. This anodic polarization corresponds to the "fatigue" noted with photo-electric effects of metals in gases, and, as in coherers for wireless, mechanical vibrations can restore the sensitiveness, or, with sufficient auxiliary cathodic polarization, the "fatigue" may be indefinitely avoided, the cell showing behaviour similar to the liquid alloy of K and Na *in vacuo*. Consideration of the photo-chemical changes of such dye-stuffs as Goldmann used to sensitize his electrodes show that both reduction and decomposition of the dye-stuff to

leuco-bodies, as well as oxidation and condensation of these to insoluble photo-anhydrides, are equally probable resultants of the illumination. The duality of the electric effect is in accord with this, and the chemical cause of the anodic polarization (or fatigue) is probably the photo-anhydride. As this increases, a current in the opposite sense to that initiating the change is installed, and this converse photo-current will be increased by light of range of frequency complementary to that exciting the primary change. Thus Luggin found that the solarization-current with his silver halide combinations was increased by red and yellow rays, which are absorbed by the photo-halide produced by blue-violet light, but transmitted by the normal halide. This is an aspect of the process we termed chromatropy, or colour-adaptation.

Discussion as to whether the process is in principle a physical or a chemical change is nugatory, it would be possible, no doubt, to give equally elegant interpretations of the original experimental fact in either language. Goldmann, following J. J. Thomson, prefers to consider a perturbation of a kinematic system of electrons as primary, and as conditioning the chemical changes.

Another way of considering the basis of the photo-electric current is to suppose that the light affects the solution-tension of the electrode, which is rather the position taken by E. Baur,[1] who worked with a combination depending upon the photolysis of uranium salts, and by M. Wilderman.[2] Wilderman uses combinations such as silver | silver halide | alkaline halide | water | water | alkaline halide | silver halide (or salt) | silver, as the chain, obtaining combinations less susceptible to polarization. He expresses the law of approach of the current to a stationary value by the equation

$$\frac{d\pi_t}{dt} = k(\pi_p - \pi_t)(\pi_t - \pi_0 + \mathrm{K})$$

where π_p is the voltage at equilibrium, π_t is the voltage at a time t, and K is an "instability-constant," introduced to allow

[1] *Zeit. phys. Chem.*, **60**, 70 (1907).
[2] *Proc. Roy. Soc.*, **74**, 370 (1904).

for hysteresis, etc. The decline of the empirical equilibrium is represented inversely by

$$-\frac{d\pi_t}{dt} = k(\pi_0 - \pi_t)(\pi_t - \pi_p + \mathrm{K}')$$

Whilst the combinations devised by Wilderman are susceptible of great reliability in action it is questionable whether the interpretation he suggests is entirely adequate. Thus he adopts as expression of the mobile photo-chemical equilibrium this generalization : " Each kind of equilibrium between two states of matter (that is, each self-consistent binary system) is, at constant volume, on exposure to light, shifted in the direction accompanied by greater absorption of light."

But there is immanent in this principle a contradiction to Wilderman's rejection of the theory of surface-forces, the ascription of the anomalies in behaviour of photo-cells to variable thickness of surface (double)-layers, as made by Becquerel, Minchin, and others, and supported by Goldmann, and, as we have previously demonstrated, supported by the mass of allied facts in regard to the anhydrous photo-electric combinations, the nature of which only differs essentially from those now under consideration in the proportion of water present. Wilderman's generalization of the mobile photo-chemical equilibrium is only sufficient up to a point. It tacitly ignores the inevitable heterogeneity of what is here too comprehensively termed "light." It would be true in the ideal limit for the force of self-propagation of a system (or molecule) capable of a pulsation between two extreme phases in the field of a discrete, homogeneous, radiation-unit *sui generis*, but it can be only approximately verified in reality, where light is inevitably heterogeneous with itself, and the actualities of selective absorption, reflection, and emission give occasion to the polarizations referred to in surface-layers of variable but definite thickness ; in other words, to the skin-effects rejected by Wilderman. What the latter has succeeded in demonstrating is the possibility of reducing these somewhat capricious forces to control and of experimentally producing reliable as well as sensitive photo-galvanic combinations. But his theoretical interpretation is inadequate, unless supported by the Planck-Einstein

postulate of discrete radiation units. Fortified by this deduction, Wilderman's generalization of the nature of photo-chemical equilibrium leads naturally to the conclusion that the forces of surface-tension, of capillarity, and the concomitant skin-effects at the boundary of heterogeneous systems, are determined by the antagonisms of radiation-units heterogeneous in period and character. The phenomena of electrode polarization in galvanic elements, whether these be thermo-electric or photo-electric combinations, are essentially surface-phenomena consisting in the formation and destruction of membranes of varying permeability for the ions, varying transparency for radiations, and in regard to the formation of which the solution-tension of an electrode (or, inversely, its polarization-capacity) is sympathetically affected by the radiation field to which it is exposed.

It follows that the generalization as to "maximum work" effected by light in a photo sensitive system deduced by Wilderman from his experiments is not conclusive without qualification. He expressed it by the proposition that "the electromotive force calculated from the photo-electric current measures the maximum work which the system can afford in light." Such principles are only valuable when definite conventions as to the meanings and experimental determinations of the several terms are adhered to, otherwise they become battlefields for profitless logomachies. Everything will depend upon what amplitude of self-closed circuit the E.M.F. is to be calculated for, since it is by definition the integral of electric force taken over a closed curve. The work of Goldmann shows that the E.M.F.'s induced by light can be analyzed into impulsive forces of momentary duration (which Wilderman prefers to disregard or compensate *inter se*) and steady forces of less rapidity but greater period of duration.

§ 137. Photo-electric Cells as Actinometers.

Wilderman recommends as very suitable combinations :—

$$(a)\quad \underset{\text{light}}{\mathrm{Ag} \mid \mathrm{AgBr}} \,.\, \frac{n}{10}\,\mathrm{BrK} \mid \underset{\text{dark}}{\mathrm{AgBr} \mid \mathrm{Ag}} \Big\} \text{ reaction } 2\mathrm{AgBr} \rightarrow \mathrm{Ag_2Br}$$

(*b*) Cu | CuO | NaOH | CuO | Cu } reaction
light dark } $2CuO \rightarrow Cu_2O$

of which the latter is in some respects preferable as giving a considerable E.M.F. for light of the same intensity over a wide range of wave-lengths, cupric oxide being black. The temperature-coefficient is small, and the constant steady maximum reached after a short induction. For a review of combinations experimented with at one time or another, see a paper by E. Kochan.[1]

[1] *Jahrb. d. Radio-aktivit. u. Elektron*, **2**, 186 (1905).

[ADDENDUM.—For a valuable paper "On the Becquerel-effect in uranium sulphate-, quinine sulphate-, and chlorophyll solutions," see K. Schaum and A. Samsonow, *Zeit. wiss. Phot.*, XI., 33 (1912).]

CHAPTER X

THE GENESIS OF LIGHT IN CHEMICAL CHANGE

§ 138. Photo-chemistry and Emission—Chemi-luminescence[1]

The statistical theory of radiation dealt with in Chap. III. has only an indirect bearing upon the specific chemical processes in which light originates. The conception of purely "thermal" or temperature-radiation is mainly a statistical idea, enabling radiation *en masse* to be dealt with on the method of averages, but incompetent alone to deal with individual chemical changes giving rise to light.

§ 139. Luminescence and Temperature Radiation.

On the basis of Kirchhoff's law, a distinction is usually drawn between temperature-radiation, and luminescence, the latter term being applied to cases in which there is reason to postulate a direct conversion of chemical or electrical energy into light without the intermediate step of adjustment of a thermal equilibrium. These independent processes extraneous to the scope of the main generalization of the economics of radiation may be provisionally classified as follows :—

Lyo-luminescence—on solution or separation of solid phases.

Tribo-luminescence—on cleavage, fracture, or breaking strain of crystals.

[1] It is somewhat regrettable that no two terms exist in English to express exactly the contrast between "Licht-reactionen" and "Leucht-reactionen" in German, the former term denoting chemical reactions induced by light-rays; the latter, chemical changes initiating concomitantly a definite luminosity, or glow, unaccompanied by perceptible rise of temperature.

Photo-luminescence { Fluorescence, Phosphorescence.

Thermo-luminescence.—This term seems in contradiction to what has been said on thermal radiation, but it refers to stimulation by heat of phosphorescence.

Electro- or cathodo-luminescence—provoked by electric discharge.

Radio-luminescence—by radio-activity.

All these phenomena may be considered as species of chemi-luminescence. Included under this head we may also add, last but not least, combustion, whether rapid or slow. The luminosity afforded by decaying organic matter in the vital processes of photogenic bacteria, fungi, and many noctilucent higher organisms pertain to this title.

Before dealing specifically and generally with the processes obtaining and the conditions contingent to the production of light in chemi-luminescence, it will be well to note the distinction accepted between fluorescence and phosphorescence. By the former is understood a re-emission of light by an illuminated medium during the excitation, apsidally to the principal axis of the incident beam, and ceasing with the excitation. It was termed by Brewster "epi-polic" dispersion, having indeed some resemblance to the scattering of light by turbid media, with which phenomenon it is indeed continuous, the two merging imperceptibly for a certain value in the "grade" or degree of dispersion of a colloid solution. That will be the more comprehensible on reflection upon the active part played by light both in condensing nuclei and in disintegrating molecules. Phosphorescence, on the other hand, or true photo-phosphorescence, to distinguish it from this kind of emission of light when the exciting cause is different, is distinguished from fluorescence by the emission proceeding subsequently to the excitation. There is an interval, as it were, of storage of light, instead of the simultaneous storage and emission during excitation effected in fluorescence, and the property is practically restricted to anhydrous bodies. Considered in their totality, the characteristic feature of all these phenomena is a mobile displacement of virtual or

self-compensating changes of a periodic nature into real irreversible ones. The importance of periodicity of intra-molecular oxidation in these phenomena has been frequently insisted on by H. Armstrong.[1] We will consider as a typical example of a fairly simple series of chemical changes concomitant with production of light, the case of the oxidation of phosphorus.

§ 140. Periodic Phenomena in the Oxidation of Phosphorus.

It was early observed that although white phosphorus combines spontaneously with free oxygen, with a luminous glow, yet increase of the partial pressure of oxygen beyond a certain value, instead of favouring the luminous trace of combustion as at first, actually extinguishes it. If, however, the mixture in this first stage of indifference be left some time in a closed vessel, the luminescence is again revived intermittently. The reaction has been studied by several observers, Joubert,[2] who first noted the periodicity, van 't Hoff and Jorissen,[3] Ewan[4] and Russell,[5] but perhaps the completest investigation is due to E. Scharff.[6] The principle conclusions are—

(*a*) There is a maximum (or rather, optimum) oxidation pressure of oxygen, beyond which the reaction is inhibited. This value differs according to the dryness of the gas.

(*b*) There is further an optimum pressure of oxygen for luminescence, or luminescence-pressure, which does not coincide with the aforementioned oxidation-pressure, being usually slightly greater. This may be due to the luminescence resulting from a breakdown of a higher, less stable oxidation stage, to a lower one.

[1] Cf. *Proc. Roy. Soc.*, **70**, 94 (1901).
[2] *Thèse sur la Phosphorescence du Phosphore*, Paris, 1874.
[3] *Zeit. phys. Chem.*, **16**, 411 (1895).
[4] *Ibid.*, **16**, 315 (1895).
[5] *Journ. Chem. Soc.*, **83**, 1263 (1903).
[6] *Zeit. phys. Chem.*, **62**, 179 (1908).

(*c*) In this condition, the state of oxidation reached is not stable in darkness, but exhibits after-oscillations and recurrent luminescences.

(*d*) These may be at once induced by lowering the oxygen pressure from that required to thus polarize the change. Upon this withdrawal of oxygen, the system again luminesces, periodically, but with diminishing momentary intensity each time, till the periods of brilliancy occur at closer and closer intervals finally giving a continuous glow of steadily diminishing intensity.

It appears likely that in this progressive oxidation process a series of oxides

$$P_4O \quad P_4O_2 \quad P_4O_3 \quad P_4O_4 \ldots P_4O_{10}$$

are formed, each conditioning a superficial or rather interfacial equilibrium, a membrane which breaks down with emission of radiation, water probably playing a definite part in the structures effected. A somewhat similar case of "periodic contact catalysis" was investigated by Bredig and Antropoff. This is the decomposition of hydrogen-peroxide by a mercury surface, when an oxide-skin of gathering tension is formed which intermittently decomposes or mechanically disintegrates, exposing a fresh virgin surface to the attack of the peroxide. The stoppage of the oxidation of phosphorus in oxygen dried with P_2O_5 suggests that a simultaneous oxidation of water to peroxide is involved in the reaction of phosphorus.

(*e*) From Scharff's observations it appears that the visible greenish luminescence starts definitely for an oxidation stage corresponding to P_4O_3, to the formation of which are ascribed the luminous clouds over oxidizing phosphorus. We can figure this as a species of quasi-homogeneous gauze, tending to form a manifold of closed surfaces or planes in which each phosphorus atom is at any $\frac{1}{4}$ period at the centre of a triangle of three oxygen atoms. The ensemble of phosphorus atoms would then form a moving continuum internal to the oxygen phase, and such that, whilst the oxygen is loosely connected up throughout by its residual (or homochemical) affinity, each phosphorus atom has at any moment

(quarter period) equal chance of contact with three oxygen atoms. The whole ensemble of light-centres forms the initial flame of phosphorus, and yields the pentoxide for a certain critical value of the pressure-gradient of oxygen. But the process is found to be catalyzed by hydrogen, or substances capable of yielding hydrogen, a certain proportion of this accelerating the adjustment of the equilibrium in the solid frame, from both sides of the reaction.

(*f*) By varying the pressure conditions of the oxidizing atmosphere in a tube containing phosphorus, many of the stratification phenomena obtained in the electric discharge through gases can be imitated.

(*g*) Influence of temperature.—The polarization pressure at which the luminescence is stopped is higher the higher the temperature. The following table exhibits the correlation between temperature, the critical luminescence pressure, p_L, and the polarization pressure, p_m respectively :—

TABLE XXXII.

Temperature.	p_L.	p_m.
15°	303·5	301·3 in mm. mercury
20°	436·8	424·3 ,, ,,
25°	451·2	448·2 ,, ,,
30°	491·2	487·2 ,, ,,
35°	520·3	515·4 ,, ,,
40°	614·9	608·7 ,, ,,
45°	640·8	633·4 ,, ,,
50°	675·8	667·3 ,, ,,
55°	701·7	689·8 ,, ,,
60°	713·7	698·2 ,, ,,

The curve is one of double flexure.

The *sulphide*, P_4S_3, shows the same phenomena, the value of p_m at 69° being 367 mm. The phenomena are similar with phosphorus itself, but divergencies occur owing to ozone formation, which displaces the oxygen pressure maximum. The luminescence pressure is here a linear function of the temperature, in the form

$$p_L = p_0 + aT$$

or

$$p_L = p_0 + T\frac{\Delta p}{\Delta T}$$

the analogy of which to the law for the photo-electric effect in the initial period will be evident (p. 374). For the temperature coefficient, Scharff found in good agreement with Joubert, the values = 23·7 and 23·1. As catalysts, certain volatile organic bodies were found effective, such as alcohols, ethers, and terpentine.

§ 141. Radiation and Nature of Flames.

This example of the photogenic autoxidation of an element, a typical metalloid, is of considerable value in suggesting conceptions likely to assist in the explanation of the nature of flames and other powerful sources of light and radiant energy. The somewhat vague notion that the emission of light from such sources was due to a conversion of heat, conceived as the *vis viva* of the molecules, into light, was early queried by Hoppe-Seyler, who considered that there was rather a direct conversion of chemical affinity into light. This view was adopted and developed in more detail by Pringsheim.[1] He considers that the emission spectra given by the salts of alkali metals, and other metals in the Bunsen flame are not to be attributed to glowing metal particles, but to the potential-gradient of the act of reduction of oxides of the metals. C. Fredenhagen[2] also considers that selective line-emission spectra are not due to isothermal temperature radiation, but essentially to valency changes. He postulates that where there is no temperature gradient, but systems in equilibrium, we get the condition for continuous spectra, but where there are specific and individual disturbances of chemical equilibrium, discontinuous emission spectra. Contrary to Pringsheim, however, he considers that the emission spectra in flames of alkaline salts are due rather to an act of oxidation

[1] *Pogg. Ann.*, **147**, 101 (1872). A comprehensive review of the problem is given in H. Kayser's *Handbuch d. Spektros.*, Bd. 1 (1900).

[2] *Ann. Phys.*, [4] **20**, 133 (1906).

than one of reduction, a thesis which he supports by the inhibition of line-emission in such sources by the introduction of chlorine. His conclusions were criticized by Paschen and others.[1] F. Auerbach,[2] from an elaborate spectroscopic investigation of the Bunsen-flame spectra, draws the following conclusions. The chlorides of Mn, Fe, Ni, and Co volatilize in the flame and become partially dissociated. It is then difficult to decide whether the line-spectra are due to electro-static actions between the metal atoms, enhancement of their residual affinities (a view somewhat similar to that expressed by Lenard[3]), and so are inter-atomic in origin, or whether they are "molecular," that is, resultant from the combination of the positive and negative elements. In a coal-gas flame fed with an air-blast, stable anhydrous oxides of the metals are formed which glow and give rise to continuous spectra. But if pure oxygen is used in place of air, the oxides are volatile and give line-spectra similar to those of the chlorides but not so rich in lines, which may be attributed to the greater expenditure of energy necessary to volatilize and dissociate the oxides. We shall return to the consideration of the nature of the processes obtaining in flames immediately, meanwhile we may notice some results obtained by M. La Rosa[4] on the relation of arc to spark spectra. In these experiments the energy exciting the radiation of the metals, etc., is supplied electrically instead of from the combustion of hydrocarbons as in the Bunsen flame. From an investigation of the singing arc, La Rosa concludes that the nature of the spectra given by an excited gas or vapour does not depend upon the mode of excitation, but on the mean energy-flux consumed per unit mass of the system. Thus arc and spark spectra are mutually convertible by variation of the wattage.[5]

[1] Cf. M. Reinganum, *Phys. Zeit.*, **8**, 182 (1907).

[2] *Wied. Ann.*, **45**, 428 (1892).

[3] *Zeit. wiss. Phot.*, **7**, 64 (1909).

[4] *Ann. Phys.*, [4] **29**, 271 (1909).

[5] On this point an important paper by Lenard should be studied (*Ann. d. Phys.*, [4] **11**, 636 (1903)). He considers that the arc consists of sheets, of which each gives a single spectral series of the given metal.

Speculation as to the identity of the emission-centres in these sources has ranged from neutral molecules and atoms to free electrolytic ions, the investigation of the electric conductivity of flames and the influence of salts upon it offering an alternative method to the spectroscopic one. Arrhenius[1] supposed that when a Bunsen flame is rendered conducting by metal salts, ions similar to those in solutions are formed. It is natural that a quantitative investigation of the nature of the conductivity, its dependence upon the actual amount of metal salt added, and the kind, magnitude, and mobility of the ions or carriers of the current should be a matter of great experimental difficulty, the overcoming of which in more recent times marks a great stride forward in the knowledge of the physics of media.

The extensive technique of the culture and control of flames in detail lies outside the purview of this work. But the word "culture" is used deliberately to signify that this technique of the study of flames must be necessarily of the same order as that of bacteriological and enzyme chemistry. Flames are not simple chemical species, but physico-chemical entities of almost biological standing in the characteristic indetermination of their nature. That is to say, they are very sensitive mobile equilibria of continuously interacting chemical species, in which the act of metathesis[2] is not subordinate to attainment of a static equilibrium, is not monotropic (in essence, exception being made of extrinsic factors which condition practical boundaries or limitations), but is the central and permanent self-reversing condition of their existence. Physically considered, flames are analogous, as singularly constituted transition or intermediate stationary motions of matter between two different states, apparently heterogeneous with each other, but really continuous in the duration of the critical intermediate medium, to "gels," which

[1] *Wied. Ann.*, **32**, 545 (1887).

[2] Meaning a double decomposition or transposition of the type AB + CD = AC + BD. For actual *adsorption* or *attraction* stages preliminary to chemical metathesis, the symbol AB : CD as first resultant of AB + CD is suggested.

present intermediate, variably permanent transitions of matter between the solid and liquid end-states, and "vapours," which present similar permanent becomings or transitions between the liquid and gaseous end-states of matter. In flames, the enduring transition of dominant photo-chemical interest is that representable by the scheme—

$$\text{gas} \rightleftharpoons \text{electrion or radiant state.}$$

And so well does the ensemble counterfeit immobility that we are likely to misapprehend the fact that the *mobility* of the transition schematized, is the essence of the fact. If we term the pulsation, the to-and-fro movement of an element of matter between two alternative, dynamically incompatible phases (such as gaseous state $\rightleftharpoons$ liquid state), a "physis" or growing, we have in "gels," "vapours," and "flames" virtually finite groups of such physes which may be termed "symphyses," expressing the fact of a multiplicity of such items growing together syntonically. And as we speak of the *maturation* of a gel, the *saturation* of a vapour, so we might speak of the *naturation* of flames.

It is essential to keep in mind the duplicity of the movements in question. The transition is not simply that of matter passing from gas to liquid (for example, taking a vapour), but of matter passing to and fro between these extremes without, so long as the virtuality of the medium is maintained, permanently remaining in either. For the maintenance of these intermediary processes, it is necessary that the antagonism of the potentials of the system in the two senses indicated should not fall outside two limits, superior and inferior. As the quantitative measure of the antagonism in question may be equally termed the measure of the equilibrium of balance of the opposite forces, it is practicably measurable as a *temperature*. The nature of heat-radiation equilibrium, and the measurement of the thermal quantities has already been touched upon. The practical and experimental side of the preparation of flames consists in (*a*) adjustment of food of the reacting materials brought to admixture in a fine state of division or dispersion, (*b*) arrangement for ignition,

(*c*) arrangement for controlling the withdrawal of the products of the process.

It has already been stated in the section on the autoxidation of phosphorus that the luminous cloud or initial flame of this reaction consisted of phosphorus and oxygen in the definite proportions P_4O_3. And we may anticipate that in all such zones of uniform radiation-quality (*vide* p. 99) the components will be present in definite proportions, but forming hylotropic phases of matter only stable between two temperature limits.

In agreement with this principle of definite composition of characteristic zones of flames (so that a flame, like a musical tone, can be either multiple or simple) we may cite the experiments of Falk[1] on the critical ignition temperature of oxygen and hydrogen. In the table are shown the ignition temperatures of given mixtures of the gases.

TABLE XXXIII.

Composition.	Ignition-temperature.
$4H_2 + O_2$	878° C.
$2H_2 + O_2$	813° C.
$H_2 + O_2$	787° C.
$H_2 + 2O_2$	803° C.
$H_2 + 4O_2$	844° C.

It is evident that a temperature minimum exists for the composition H : O or $H_2 : O_2$, and this, corresponding conversely to maximum entropy for an invariant heat-energy volume (the radiation or action-unit of Planck-Einstein's theory) accords with the conception of hydrogen peroxide as the initial flame-zone of these elements, water and oxygen being by-products of an isolated encounter, such as[2]—

$$H_2O_2 + H_2O_2 \rightarrow \dot{H}_2O_2 : H_2O_2 \gtrless 2H_2O + 2O_2$$

to accomplish this *isolation* being the function of catalysts

[1] *Ann. Phys.*, [4] **24**, 450 (1907).

[2] The scheme $H_2O_2 : H_2O_2$ denotes the preliminary adsorption-step.

accelerating the decomposition of hydrogen peroxide. In the case of carbon monoxide, the ignition temperature minimum was that correlative to the reaction

$$2CO + O_2 = C_2O_4$$

that is, the formation of the anion of oxalic acid, but the existence of formaldehyde H·CHO at the edge of this flame is very probable. It should be noticed that these results were for adiabatic constant volume conditions, in which the flame is enclosed in a solid receptacle, and that under such a condition excess of either component raises the ignition temperature and impedes the reaction.

§ 142. Figure and Form of Flames.

The figure, form, and extension enforced upon a flame will in practice depend upon the use it is required for, and particularly whether it is desired to use or study it as a heat-source or as a light-source.

As the majority of flames consist of combustible substances brought to the gaseous condition and burnt in air, the figure of the flame is largely conditioned by the channel and orifice by which it is fed to the air. The simplest case is when the gas streams under uniform pressure through a narrow-bore tube into the atmosphere, when the flame presents a more or less elongated double cone or cylinder, tapering somewhat at top and bottom, and somewhat the same conditions, dynamically speaking, obtain as regards its stability as for a liquid jet.[1] In the case of the jet, the stability is a function both of the kinetic energy of the stream and of the surface tension of the liquid, whilst in a flame it is the interfacial tension between the substance in the gaseous and the radiant or electrionic state which takes the place of surface-tension in the liquid analogue. The linear dimensions of a flame are dependent upon a balance between the pressure of outflow of one component or mixture, and the external pressure of the atmosphere.

[1] Cf. any text-book of physics, *e.g.* Poynting and Thomson, *Properties of Matter*, p. 151; and Rayleigh, "On the Stability or Instability of certain Fluid Motions," *Sci. Papers*, V. i. 474.

Suppose the latter to be constant, and not considering for the moment the specific chemical nature of the components, there will be a certain maximum outflow-pressure, and a certain maximum velocity of outflow beyond which the flame will tend to detach itself, this pressure being probably coincident with the so-called fugitive or transient pressures in explosions[1] and travelling either in the explosion-wave itself or in the compression-wave preceding it. Calling the maximum efflux-velocity C, and p the maximum efflux pressure, then $C = k\frac{dp}{dt}$. Mache,[2] working with coal-gas and air, has determined the value of C for different percentage compositions :—

TABLE XXXIV.

Per cent. coal-gas.	c $\frac{\text{cms.}}{\text{sec.}}$	C $\frac{\text{cms.}}{\text{sec.}}$	$\frac{C}{c}$
10·53	19·9	107	5·4
11·56	23·2	222	9·6
12·14	25·0	433	17·3
14·39	32·2	559	17·4
14·72	33·2	653	19·7
15·26	34·9	733	21·0
15·62	36·1	880	24·4

In this table, c gives the normal explosion-wave velocity by the method of Michelson and Gouy,[3] whilst C is the maximum explosion-velocity, which Mache considers to determine the limit of stationary existence of the flame. As regards the localization of the currents in the flame, which tend to form a series of shells or equipotential surfaces, Mache found that on introducing carbon-dust into the gas-stream of a Bunsen flame the glowing particles follow paths parallel to the outer contours of the flame, forming an angle with the inner nearly true cone, which he registered photographically.

[1] Cf. J. W. Mellor, *Chemical Statics and Dynamics*, this series, p. 483.

[2] *Sitz. ber. k. Akad. Wiss. Wien.*, **106** (II*a*.), 1081 (1907).

[3] For details as to the determination of explosion velocities, see Mellor, *loc. cit.*

§ 143. Ionization in Flames.

Another method of investigating the structure of the flame consists in the introduction of metallic salts and measuring the mobility of the ions under a known potential gradient. The first quantitative datum of importance as to this conductivity was obtained by Arrhenius.[1] He found that the conductivity was proportional to $\sqrt{m}$, where m is the amount of metal salt inserted. Deviations from this obtain, however, for large quantities of salt, high values of m, the original parabolic rate of increase of conductivity yielding to a slow linear rate.[2] The principal researches subsequent to that of Arrhenius upon this problem are due to Smithells, Dawson, and H. A. Wilson,[3] and to P. Lenard[4] and his fellow-workers. Details of the methods of measuring the conductivity, and formulæ for computing the masses and mobilities of the carriers, positive and negative, will be found in papers by Lenard and E. N. da C. Andrade.[5] Lenard and Andrade conclude that the conductivity of flames containing salts of the metals is due—considering only electrodeless flames—in the first instance to collisions between metal atoms, which then set free electrons by the working of proximity ("Nähewirkung"). This action is assumed to occur similarly in solid metals, so that whenever two metal atoms come sufficiently close together they liberate one or more electrons, becoming positively charged in consequence. The emission of light is ascribed by Lenard principally to the collision of the metal atoms with molecules of the flame-gases, rather than to the return of the liberated electrons to the metal atoms. But it is feasible, it is argued, that this interaction of the metal atoms with the gas-molecules is also dependent upon a temporary liberation and recoil of electrons.

[1] *Wien. Ber.*, July (1890).

[2] Smithells, Dawson, and H. A. Wilson, *Phil. Trans.*, A. **193**, 89 (1900).

[3] *Phil. Trans.*, A. **193**, 89 (1900).

[4] On the conductivity and light-emission of flames containing metals, *Sitz. ber. Heid. Akad. Wiss.*, Abh. 34, 1 (1911).

[5] *Phil. Mag.*, June, p. 865 (1912), and *ibid.*, July, 1912, p. 15.

Whatever be the explanation of the actual emission, an important discovery, due to Lenard and confirmed by Andrade, is that the carriers are continually alternating the charged or electrionic condition with a neutral condition. Andrade has shown, not only that the positive carriers in such loaded flames are metallic in nature, and probably metal atoms, but that they have two definitely different velocities of migration in an electric field, according to whether present in a luminous streak of metallic vapour or in the rest of the flame. In both cases they alternate between the positively charged and the neutral state, in the former case being charged for only $\frac{1}{400}$ of the time, in the latter $\frac{1}{6}$. There exist, beside the free electrons, negative carriers of greater magnitude, in relatively small numbers, which are metallic in their nature, a condition of things analogous to that of canal rays. When it is remembered that not only the elements of the anion of the salt are probably present in the flame, but also carbon, oxygen, nitrogen, and a variety of more or less loosely combined residues of these, it is evident that several possible factors liable to affect discontinuously the migration of carriers exist in the flame.

Lenard's theories as to the nature of the processes concerned in the emission of discontinuous series-spectra by the metals will be referred to again under phosphorescence. The spectroscopically distinguishable zones in a hydrocarbon-oxygen flame (Bunsen flame) have been investigated by C. de Watteville and others, and are easily observed with the naked eye in an ordinary laboratory burner.[1] They consist in an inmost bluish zone where unburnt hydrocarbon is yet in excess, an intermediate zone, which is, so to say, the pure flame wherein oxidizing and reducing activities counterbalance, and an outer virtually colourless shell, which contains excess of oxygen, and that indeed in some part in a very "active" condition. It is this part of the flame which is most easily coloured by metallic salts, and the possibility of oxygen playing a considerable part in the processes there is not to be denied weight.

[1] Cf. G. Urbain, *Introduction à la Spectrochimie* (Paris, Hermann et fils, 1912). The inner cone is actually a stationary explosion-wave.

§ 144. Phosphorescence.

Historically considered, many varieties of luminescence and more or less faint and fugitive light-production have been included at one time or another under the term "phosphorescence." One will call to mind the luminosity produced by certain marine infusoria, by photogenic bacteria and fungi, and, considering the continuity and concomitance of the decay and decomposition of one set of organisms in Nature's cycle with the growth and increase of others, what probably therefore refers to the same facts as these just mentioned, namely, the decay in putrefaction of organic matter. But such phenomena of slow combustion in organic media may well be distinguished from the phenomena of inorganic phosphorescence which we shall specially apply to the emission of light by certain inorganic systems subsequent to excitation by light. The more important of these bodies contain no water, which furnishes another distinguishing feature from the organic processes, where the material is strongly hydrated.

Although light is perhaps the most interesting agent of excitation, phosphorescence in suitable material may be excited in a variety of ways. Thus we may have—

(*a*) Phosphorescence due to visible light.
(*b*) „ „ ultra-violet rays.
(*c*) „ „ cathode rays.
(*d*) „ „ Röntgen rays.
(*e*) „ „ mechanical shock and heat, though these, as distinct from ordinary thermal emission of light, actually consist in a revival of photo-phosphorescence.

§ 145. Discrimination and Study of Phosphorescence.

The principal difference between fluorescence, if a rigorous distinction be insisted upon, consists in the duration and actual persistence of an effect. Phosphorescence is usually applied to an after-glow subsequent to excitation, though its

duration may be very brief, phosphorescence of $\frac{1}{5000}$ second having been observed. Whereas in fluorescence there is a transformation and redistribution of radiation about a new optical centre of gravity which is concomitant with the actual excitation. The study of phosphorescence was first raised to a quantitative level by E. Becquerel,[1] who not only investigated the preparation of phosphors but designed several phosphoroscopes to deal with emissions of short duration. The principle these are based on is simple. Two rigid discs are mounted on a common axis, at a certain distance apart. In each disc, four angular apertures, of 22° 30′, are cut, the four apertures forming a cross. The two discs are so arranged that the apertures do not face each other, but the interspaces of the one shield the open spaces of the other. Owing to the great velocity of light, it would evidently require an enormous velocity of rotation, some $2 \cdot 10^{10}$ revs. per sec., to let an impinging ray pass through. The phosphor is placed between the two, is illuminated from one side, and viewed by its own luminosity. It can then be exposed to a series of intermittent illuminations of period determined by the rate of revolution of the discs, and examined under conditions symmetrical with those under which it is exposed. Becquerel terms the mean time interval that between the instant when insolation ceases to the instant when the observer perceives the body in the midst of the aperture. The arrangement just described is suitable for observing the phosphorescent light transmitted by a very thin layer, but the apparatus can readily be adapted to work by reflection.

Instead of the unarmed eye, a spectrometer, spectrograph, or photometer may be used for the examination. By means of this instrument the number of substances recognized as phosphorescent has been greatly extended, although many of them only phosphoresce for a very brief period after exposure.

Wiedeman[2] improved upon Becquerel's instrument and made the calculation of the time-intervals more correct.

[1] *La Lumière*, I., 248 *et seq.*

[2] *Wied. Ann.*, **34**, 446 (1888). Cf. Sir W. Crookes, *Proc. Roy. Soc.*, **42**, 111 (1887).

When cathode rays, or the spark discharge, are used to excite phosphorescence, simpler means of regulating the exposure may be employed.[1] Lenard made the arm of a Foucault contact-breaker, used with an induction-coil, act as an intermittent shutter to a spark-gap which was the source employed.

§ 146. Chemical and Physical Nature of Phosphorescent Systems.

Although so frequent, when properly sought after, as to deserve the title of a general property of matter, we shall restrict our attention to certain preparations in which the property is peculiarly developed and very intense in operation, and which are therefore calculated to exhibit the fundamental conditions essential to its manifestation. These preparations have in consequence been emphatically entitled "phosphors."[2] Phosphorescence is predominantly a phenomenon of matter in the solid state and indeed of systems produced under great adiabatic compression.

Phosphors are artificially produced by roasting with charcoal sulphates of the alkaline earth and allied elements.[3]

Methods of preparation are described by E. Becquerel,[4] by Lenard and Klatt,[5] and by P. Waentig.[6] The roasting of the sulphate with carbon effects a partial reduction to sulphide. But it was first clearly shown by Lenard that pure sulphides of the alkaline earths do not phosphoresce; for this to come into full play, it is essential that traces of metals such as Cu, Bi, Mn, Pb, Ag, Zn, Ni, Sb, should be present in a very finely divided state, or in solid solution. Waentig considers that under

[1] P. Lenard, *Wied. Ann.*, **46**, 637 (1892); C. de Watteville, *C. R.*, **142**, 1078 (1906).

[2] The element phosphorus was at first considered to be a peculiarly strong phosphor.

[3] On naturally occurring phosphors or luminous stones, see H. Kayser, *Handbuch d. Spectroscop.*, Bd. 1.

[4] *C. R.*, **103**, 468, 629.

[5] *Wied. Ann.*, **38**, 90 (1889).

[6] *Zeit. phys. Chem.*, **51**, 435 (1905).

ordinary conditions, at temperatures and pressures that is to say much below those at which the phosphor is engendered, the systems are supersaturated with regard to the metal, and in a meta-stable condition. The quantities of free metal necessary to confer a vivid phosphorescence may be extraordinarily minute; only 0·000005 gram of Cu is necessary for the evolution of the copper bands in a barium sulphide phosphor, which is considerably more sensitive than the majority of analytic tests for copper.

As was pointed out by previous experimenters, and confirmed by Lenard and Waentig, there are three components essential to a powerfully reacting phosphor. These are (*a*) the alkaline earth sulphide, (*b*) minute traces of certain active metals, (*c*) a flux or fusible addition, usually a salt such as Li_3PO_4, Na_2SO_4, Na_2F_2, etc. This last helps the dissolution of the metal to a homogeneous distribution in the mass on fusion, and assists in retaining it on cooling when the system is in a quasi-vitreous condition. The result is to form a system of minute electrodes or centres of varying tension embedded in a material of high dielectric capacity.[1]

The unique importance of small traces of those metals which show more than one valency-stage and are usually associated with the development of colour in inorganic media and in solutions of their salts and compounds, was first clearly indicated by L. de Boisbaudran[2] and Verneuil.[3] That the conditions of phosphorescence are very complex and indeterminate will be evident from L. de Boisbaudran's conclusions.

(i.) The same solvent, *e.g.* earth sulphide, may be functionally active for one and not for another nearly related element.

(ii.) Strongly coloured substances are unsuitable as solvents.

(iii.) The same substance may be a passive substratum in one case, an active inductor in another.

[1] Cf. P. Lenard and V. Klatt, *Ann. d. Phys.*, **15**, 225 (1904), and B. Winawer, *Inaug. Dissert.* (Heidelberg, 1909).

[2] *C. R.*, **105**, 345 (1887).

[3] *Ibid.*, **104**, 501 (1887).

(iv.) Two active substances when compounded in the same system may inhibit each other's activity without apparently undergoing chemical combination.

But for all the complexity of the problem it has been increasingly brought into the domain of quantitative control and determination, an advance due in a large degree to the work of Lenard and his colleagues.[1] In this the spectroscopic and spectrophotometric investigation of the luminescence, as well as the determination of the time-rates of its growth on excitation and decay after, have given the necessary numerical reduction of the problem in a great many cases.

§ 147. Spectroscopic Nature of the Phosphorescence.

In general, the light is found to consist of well-marked bands, of greater or lesser intensity and degree of dispersion (for the same registering system, of course) according to the energy of the excitation. That phosphors give a light peculiar to their constitution and independent of the nature of the exciting light was shown by Dufay and Wilson in the eighteenth century. But it is important to notice that bands which may be allocated to a certain metal in a phosphor are subject to modification according to the nature of the anions present. Thus Becquerel[2] found marked difference in the banded spectra given by uranium salts according to the acid radicle present. Certain naturally phosphorescent bodies, (fluorspar and chlorophane) show the spectra of many rare earth elements if these are mixed with them.[3]

Lenard and Klatt[4] have made extensive investigations of the spectra given by the artificial phosphors of the alkaline

[1] *Wied. Ann.*, **38**, 90 (1889); *Ann. Phys.*, [4], **15**, 225, 445, 633 (1904); [4] **28** (1909), p. 476; [4] **31**, 641 (1910).

[2] *La Lumière*, *loc. cit.*

[3] Cf. G. Urbain, *C. R.*, **143**, 825 (1906), and *Introduction à l'Étude de la Spectrochimie* (Hermann et fils, Paris, 1911). Further, E. C. C. Baly, *Spectroscopy*, this series, and W. J. Humphreys, *Astrophys. Journ.*, **20**, 256 (1904).

[4] *Loc. cit.*, p. 400.

earth sulphides impregnated with metals. Each phosphorescent spectrum, however excited, consists of fixed groups of bands more or less independent of each other, peculiar to the active metal. The visibility of the different bands depends upon—

(*a*) The temperature the phosphor is maintained at.

(*b*) The nature (quality and intensity) of the radiation used to excite it.

(*c*) The time after excitation that the stimulus is observed. Different bands are discriminated by having very different rates of decay, and different behaviour with respect to temperature, a *band* being defined as a complex of waves having common properties in respect of temperature, excitation by light, and rate of decay.

§ 148. Dynamics of Phosphorescence.

In general, with reservations which affect the original rule also, it may be said that a law akin to Stokes' law for fluorescence holds for phosphorescence, to the effect that the excited radiation has its optical centre of gravity further toward the longer wave-lengths of the spectrum than that of the exciting radiation. But as already stated, the excited radiation is much more specifically characteristic of the phosphor than a mere reflex of the incident rays. Of fundamental importance in considering the nature of the emission and the conditions of its persistence is the antagonistic effect of rays of different period. This is peculiarly evident in the inhibiting or extinguishing effect upon phosphorescence which is effected by red and infra-red rays. Ritter[1] first noticed that not only did red and infra-red rays possess little or no power of stimulating phosphorescence, but that if they were allowed to impinge upon a body already phosphorescing, they could actually quench the light-emission. This phenomenon was rediscovered by Becquerel and turned by Draper[2] to the

[1] See H. Kayser, *Handbuch d. Spectros.*, Bd. 4, p. 794.

[2] *Phil. Mag.*, [5] **11**, 157 (1881).

evolution of a method of phosphoric-photography of the infra-red region of the spectrum. Becquerel noticed that the quenching action of the infra-red did not take place instanter, but that at first the brightness was rather increased. Stokes showed further that the increase at this stage was due to light of different spectral composition.[1]

Wiedeman and Schmidt[2] also investigated the extinction-phenomenon, and found that phosphorescence excited by rays from a spark-gap could be quenched by infra-red rays.

§ 149. Brightness and Intensity-values.

It will be evident that considerable difference of opinion and interpretation in such phenomena where there is a varying function is likely to occur through different observers taking different definitions of brightness and intensity. We may distinguish in regard to the energy-yield in a given band, between momentary brightness and integral intensity.[3] The fraction of the integral intensity which is observable in the mean time-interval of an individual's perception is then momentary brightness, the brightness for a moment observed from moment to moment. There is a certain proportionality between the photometric brightness of the exciting rays (which, for constant light-source, may be regarded as directly proportional to its intensity) and the photometric brightness of the phosphorescence stimulated, but no simple correlation holds over a wide range. Further researches by Dahms,[4] however, show that the same infra-red rays may either quench or speed-up a light-centre in a phosphor, according to the state of the latter. Lenard has shown recently[5] that the total light-integral (Lichtsumme) emitted is the same, whether the emission is affected

[1] *Proc. Roy. Soc.*, **34**, 63 (1882).

[2] *Wied. Ann.*, **56**, 201 (1895).

[3] Cf. P. Lenard, "On the Emission of Light (in Phosphors) and its Excitation," *Sitz. ber. d. Heidelberg, Akad. Wiss.*, Abh. 3 (1909).

[4] *Ann. d. Phys.*, [4] **14**, 215 (1904).

[5] *Sitz. ber. Heid. Akad.*, 1912.

by infra-red or not. Nichols and Merrit [1] state that with sidot-blende (phosphorescent zinc sulphide) there is an approach to a saturation stimulus in the excited phosphor, the brightness upon excitation as the intensity of the exciter is greatly increased, only increasing slowly above a certain value. Their investigation, no less than those of Lenard and Klatt [2] showed that no simple or uniform law holds for the emission in its totality, but each spectrally distinct band possesses, under determined conditions of temperature, its own susceptibility by excitation and its own manner and rate of passing away. For this dying-down of the phosphorescence we shall use the term "decay," although it is perhaps not the most suitable. In illustration of the phenomena to be observed, the following table from Lenard and Klatt is given. At the head of the table is given the earth-sulphide and the metal; the *intensities* given in the third column were in this case only eye-estimates according to a scale of eight steps.

Intensity *i.*1 is too weak for the colour to be distinguished, *i.*2 such that the colour just appears, *i.*4 is what a well-rested eye in a darkened room would term a bright light, *i.*6 is a luminosity showing coloured in an undarkened room, *i.*8 strong enough for several such surfaces to make reading possible in an ordinary room. These estimates were made one second after cessation of insolation, they are of course quite rough, but afford a good preliminary orientation in respect of the visibility of the appearances. Column 5 refers to the decay of the phosphorescence, or more generally, to its duration, the persistence and decrease thereof. A very persistent phosphorescence in this case was one which was still visible after some hours.

[1] F. E. Kester, *Phys. Rev.*, **9**, 164 (1899).
[2] *Phys. Rev.*, **23**, 37 (1906).

TABLE XXXV.—CA-SULPHIDE WITH CU.

No.	Addition.	Intensity.	Colour.	Course of decay.
1	Na_2SO_4	4	Green	Little copper
2		4	Blue-green	With more Cu ; fairly persistent, greener with time
3	$Na_2S_2O_3$	4	Blue-green	Ditto
4	$NaHPO_4$	4	Blue-green	Ditto
7	Li_2SO_4	4–5	Bright blue	Becoming green, with little Cu
8	—	4–5	Green-blue	
9	Li_3PO_4	4	Turquoise	
10	$Li_2B_4O_7$	4	Turquoise	
11	Li_2SO_4 plus $CaFl_2$	5	Turquoise	Persistent, becoming greener
12	K_2SO_4	2	Deep blue-violet	Impermanent, seen sinking below *i*. 1

For a very comprehensive and detailed description of a vast number of such phosphors and their characteristics, the series of papers by Lenard and Klatt, frequently referred to here, should be studied.[1]

§ 150. CALCULATION OF INTENSITY-LAWS.

Becquerel[2] was the first to attempt a quantitative theory of the rise and decline of phosphorescence. He started from the postulate that a phosphor had a certain definite light-capacity, saturation or susceptibility S (it may be mentioned that there is a considerable analogy between the phenomena of excitation and stimulation of phosphors, and the magnetization of steels), and a certain emissivity E for its own particular light. The actual emission $\frac{di}{dt}$ may therefore be written

$$\frac{di}{dt} = f\left(\frac{E}{S}\right) \quad .$$

[1] *Wied. Ann.*, **38**, 90 (1889) ; *Ann. Phys.*, [4] **15**, 225 (1904) ; *ibid.* 425 ; *ibid.* 634.

[2] *La Lumière*, *loc. cit.*

where E is the emissivity, S the susceptibility. As regards the form of the function f, if we assume a law similar to Newton's law of cooling, we have

$$\frac{di}{dt} = -\frac{E}{S} = -ai, \text{ when } a = \frac{E}{S} \text{ lim.}$$

Hence an ordinary exponential law is obtained

$$i = i_0 \cdot e^{-at}$$

which was found valid for certain phosphorescences of short duration. For more persistent ones, Becquerel found the empirical formula

$$i^m (k + t) = k i_0^m$$

where i_0^m can be put equal to unity for a selected example, fairly adequate. H. Becquerel[1] has shown that this formula can be obtained from the ordinary differential equation for forced vibrations, when a friction term is present with the friction set proportional to some power of the velocity. Supposing this to be the second power, we have

$$a\frac{d^2u}{dt^2} + \beta u \mp \gamma\left(\frac{du}{dt}\right) = 0$$

where u is the amplitude of vibration. A general solution of this is

$$u_n = \frac{u_0}{1 + u_0 \cdot 4/3\gamma \cdot n}$$

where u_0 is the amplitude of the nth, u_0 of the *first* (of zero order) vibration.

Considering the intensity as the mean square of the amplitude, and that n, the number of vibrations, can be regarded as proportional to time, we have

$$u = \frac{u_0}{1 + u_0 bt} = \sqrt{i} = \frac{1}{a + bt}$$

which is the same as E. Becquerel's formula, for the case of $m = \frac{1}{2}$. Regarding m as a statistical index of correlation of

[1] *C. R.*, **113**, 618 (1891).

intensity and *time*, the constants a and b are regression-coefficients, and may differ from band to band. Thus H. Becquerel found for the two bands of a copper-calcium sulphide phosphor

$$i = \frac{1}{(57 + 0{\cdot}09t)^2} + \frac{1}{(7{\cdot}97 + 0{\cdot}65t)^2}$$

Micheli[1] made experiments at different temperatures and found from 20° C. downward, the formula it = constant held very well in several cases up to 66 minutes. Buchner,[2] using a photographic plate obtained quite different results, which is to be expected from the very different spectral sensitiveness possessed by the plate compared with that of the eye. Not only, as Lenard and Klatt and others have found, is the phosphorescent light observed from moment to moment a sum of effects due to two or more bands with different time-rates of variation, but A. Werner[3] was unable to find any single-valued function expressing the persistence of one band in all stages. He considered that on cessation of the insolation, the stimulus in the phosphor (what we may call by a physiological analogy its photo-tonus) resolves itself into two effects, one a rapid emission, giving an exponential rate of damping of the moment-intensity of the band, and a much slower process, corresponding to a species of permanent set in the light-centres of the phosphor, this latter is fairly well represented by Becquerel's formula—

$$i^m (a + bt) = k$$

Werner measured the intensity-decay of the α-band, $\lambda = 550\ \mu\mu$, of Sr-Zn-(CaF_2) phosphors. The influence of illumination was represented by a curve rapidly attaining a saturation-value (*cf.* the curves for the photo-electric current), the saturation-intensity then falling off somewhat on more prolonged exposure, which may be attributed to the quenching effect of the rays of longer wave-length coming into play.

[1] *Arch. Sc. phys. et nat. nèer.*, [4] **12**, 5 (1901).
[2] See H. Kayser, *Handbuch d. Spectros.*, Bd. 4, p. 721.
[3] *Ann. Phys.*, [4] 24, 164 (1907).

With increased intensity of the source, the phosphorescent-intensity at first increased nearly in direct proportion, but gradually reached a limiting value.

For the decay of the total brightness (Lenard's "Licht-summe") curves were obtained which could be represented neither by an exponential function nor a parabolic one, but could be regarded as compounded of the superposition of a rapid exponential decrease with a slow linear regression representable by Becquerel's expression in the form—

$$\frac{1}{\sqrt{i}} - \frac{1}{\sqrt{i_0}} = \frac{t}{T}$$

T being the time-constant of their persistent process, i_0 its initial intensity. On the other hand, the momentary process (giving what Lenard terms a "Momentanband") follows a function of the form—

$$I = I_0 e^{-at^n}$$

where n depends upon the exciting intensity. Werner concludes that the initial intensity i_0 of the *persistent* process is a measure of the light-storage effected, and that this persistent process is effected by a different region of the spectrum to that exciting the momentary one. Taking the ratio of initial intensities of these, as near the moment of cessation of excitation as possible, then this ratio $\frac{i_0}{i_0}$, $\frac{\text{momentary}}{\text{persistent}}$ effect, is for the same phosphor greater for cathode rays of low intensity, or quartz-filtered ultra-violet, than for cathode rays of great intensity.

The superior efficiency of cathode rays in provoking phosphorescence and cathode-luminescence leads readily to the coupling of phosphorescence with the photo-electric effects previously noticed. It is in virtue of such an assimilation that P. Lenard has founded his theory of phosphorescence. But before introducing this or other conceptions of the inner mechanism of the process, we may note that in the course of their investigation of the photo-electric effects given by phosphors, Lenard and Saeland [1] observed an allied action of

[1] *Ann. Phys.*, **28**, 476 (1909).

light upon the phosphors, which they termed "actinodielectric action." It consists in a partially or completely reversible dielectric displacement in the phosphor when this is simultaneously exposed to red or infra-red light, and to an electric field in which its dielectric constant (specific inductive capacity) is determined. This reversible breakdown of the insulating power of the phosphor when exposed to light was further investigated by C. Ramsauer, W. Hausser, and R. Oeder.[1]

§ 151. Theories of Phosphorescence.

(*a*) The earliest conception of the process may be called the "sponge" hypothesis. It was based on the prevalent theory of a substance "light," and supposed that the phosphor absorbed light like a dried sponge does water, giving it out again in darkness as if under some form of inner pressure.

(*b*) The next theory worthy of note, and which was supported by Becquerel and Wiedeman, supposed that the phosphorescence was a consequence of pulsation or oscillation of the particles of the phosphor between two conditions or states. Roughly representable by the scheme—

$$\rightarrow \text{light} + \text{A} \rightarrow \text{B}$$
$$\text{B} \rightarrow \text{A} + \text{light} \rightarrow$$

this hypothesis, especially when modified by the assumption (if required) of more than one kind of vibrating molecule, responsive to more than one train of light-waves, readily suggests a mathematical formulation of the kinetics of the action, without being committed to any very explicit picture of the dynamic.

(*c*) A chemical theory of the process is that it consists in a periodically retarded and accelerated process of slow or persistent combustion, both hydration (and dehydration) and intramolecular autoxidation being concerned. Rays from one region of the spectrum accelerate one aspect of the process, rays from another retard this aspect, in that they accelerate the alternative side of the change. This theory is not incompatible

[1] *Ann. Phys.*, [4] **34**, 445 (1911).

with the preceding, nor with the later ionic and electronic theory, it simply lays more stress on the chemical aspects of the problem.

(*d*) Electronic and ionic theories.

It is natural that phosphorescence should have been drawn into the dominion of the amber witch, electricity, and explained in terms of gyrations and terpsichorean antics of her elves and fays, the ubiquitous electrons and ions. De Visser[1] suggested that in the phosphor, considered as a solid solution of a metal or a metal group, the electro-magnetic vibrations of light increased the amplitude of vibration of the quasi-bound electrons of the metal till they became detached from the electrions, or atomic electric fields, of which they formed part. On cessation of the exciting rays, these electrons returned to their nuclei, but meeting with inert or neutral molecules, raised these to momentary incandescence.[2] The most consequent development of the electron theory—the theory of discrete, atomic quantities of electricity, with which is associated the Planck-Einstein theory of finite action and radiation-units—in regard to phosphorescence is due to Lenard,[3] who points out forcible reasons for regarding the processes of emission of series spectra by excited metal vapours, and the luminescence of phosphors as processes of a kindred order in the metal atoms in question.[4] In both cases Lenard postulates an expulsion of electrons from the atom, and light-emission consequent on their return. If the using-up or dissipation of the acquired stimulus consists in a return of the electrons with an oscillating approximation to their original orbits in the sphere of influence or dynamid of the atom, as the possibility occurs of a consequent electric current in the space occupied by the emission centre, this nucleus may consist of more than one

[1] *Rec. trav. chim. Pays Bas.*, **20**, 435 (1905).

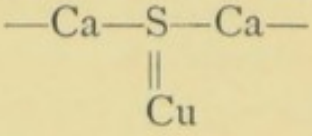
[2] Cf. also J. de Kowalski, *Bull. Akad. Sci. Cracovie*, p. 649 (1908).

[3] A summary of his views will be found in a paper "On the Emission of Light and its Excitation," *Sitz. ber. Heidelberg, Acad. Wiss.*, Abh. 3 (1909); also *Ann. d. Phys.*, [4] **31**, 641 (1910).

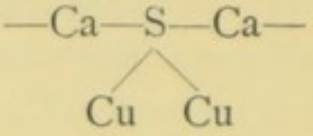
[4] That exactly the same wave-lengths are active in producing photo-electric effects and exciting phosphorescence in the same phosphor was shown by Lenard and Saeland. *Ann. d. Phys.*, [4] **28**, 476 (1909).

metallic element, which Lenard suggests are grouped about a sulphur atom, *e.g.*

In the CaCu α *d*-centres[1]



In the CaCu β *d*-centres



the terms α *d*-centres and β *d*-centres referring to the corresponding persistent ("Dauer") bands, the bands emitted by the centre in two conditions differing according to the number of valency-electrons they have lost. The inner current referred to would then depend upon the chemical composition of the phosphor, and would further depend in general upon temperature in a manner corresponding with the actual three temperature stages of the bands.

§ 152. Excitation Distribution and Temperature.

Experiments over a very wide range of temperature, from that of liquid hydrogen upward,[2] show that each band, on increase of temperature, gives three states or conditions. These are termed the "cold state" or lower momentary state, the permanent or persistent state, and the "hot state" or upper momentary condition. In the first, only storage of energy occurs, without after-glow; in the second, both storage and after-glow; in the third, neither.

The momentary luminescence, which may occur for any stage, and during the excitation, is properly speaking fluorescence. That the same atomic groups are capable of either fluorescence or momentary luminescence, or the persistent luminescence of phosphorescence proper, rather according to the medium immersed in and its conditions of pressure and temperature, than the original source of excitation, is shown

[1] In order to account for the same centre being able to give more than one band, it is assumed that the nature of the linkage of the active metal-atom with the sulphur-atom may differ from time to time. In support of this there is the fact that there are never more bands than the active metal has valencies.

[2] P. Lenard, *loc. cit.*, 1904.

by the fact that dye-stuffs, fluorescent in liquid solutions, can be made to exhibit persistent after-glow and the criteria of phosphorescence proper, if dissolved or dispersed in a solid or semi-solid medium.[1] The following table exhibits some of Schmidt's results on this point; his work also showed the close correlation of the luminescence spectrum with the absorption spectrum.

TABLE XXXVI.

System.	Colour.	$\lambda_1 - \lambda_2$, limits of band in $\mu\mu$.
Fuchsin in gelatine . . .	Yellow	665 to 554
Rose-bengal in gelatine .	Yellow	670 to 540
Chrysanilin in gelatine . .	Yellow-green	690 to 480
Methyl violet in gelatine .	Red	680 to 590
Fuchsin in phthalic acid .	Yellow-green	610 to 485
Auramine in sugar . . .	Green	590 to 490

Similarly, all organic bodies possessing strongly marked absorption bands in the ultra-violet seem capable of either fluorescence in a dispersed condition or phosphorescence in a condensed condition, when excited by radiant energy of sufficient frequency. Examples are retene, anthracene, hydroquinone, phenol, etc.

§ 153. FLUORESCENCE OF METALLIC VAPOURS.

The fluorescence of metallic vapours in vacuo or generally under greatly reduced pressure of oxidizing gases, pertains properly to spectroscopy, and is only briefly dealt with here on account of the complementarity of emission processes with the absorption and photo-chemical activity of light. Remarkable results have been obtained on the dispersion of light by sodium vapour kept at a high temperature in a good vacuum (as regards other elements) and excited with light of different kinds.[2] A diagrammatic representation of Wood's arrangement is shown in Fig. 45.

[1] G. C. Schmidt, *Wied. Ann.*, **58**, 103 (1896).
[2] R. W. Wood, *Phil. Mag.* (1906).

In the horizontal tube, of porcelain or steel, were heated pieces of sodium. The end of the tube is provided with a quartz window, through which light is introduced at oblique incidence to the axis of the tube, and the fluorescence excited in the heated vapour is then examined with a spectroscope, the optical axis of which is also inclined to that of the tube. The actual spectroscopic phenomena are very complex and only some of the salient results are referred to here.

(*a*) The fluorescent and the absorption spectrum are complementary.

(*b*) Excitation with the sodium D_1–D_2 lines produces a pair of the same wave-lengths in the luminescent spectrum, but also

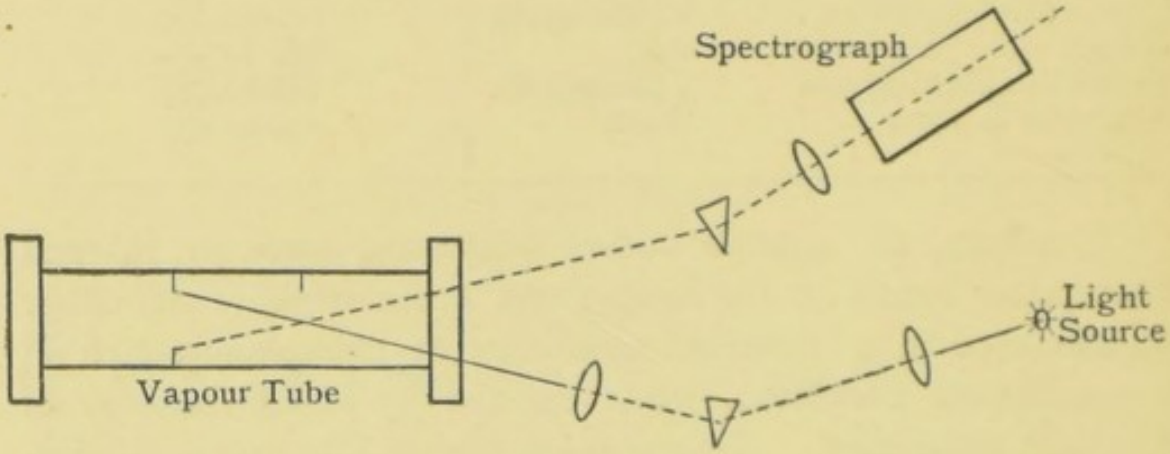


FIG. 45

bands of lower refrangibility. The D_1–D_2 lines do not appear if light of those wave-lengths is absent from the exciting beam.

(*c*) Violet light had little apparent effect, but on passing toward the longer waves (in the exciting beam) a yellowish fluorescence is developed, composed partially of reflected or readmitted incident rays, and a further refracted group. As the exciting beam, or rather its spectral centre of gravity, is displaced toward the longer wave-lengths the head of the fluorescent spectrum is progressively displaced in the contrary sense, there being always a certain amount of overlap and direct re-emission of exciting rays as well as transformation.

Stokes' law (*vide* p. 416) is practically abrogated, particularly when the optical centre of the exciting light is near the principal mode of the luminiscent spectrum.

(*d*) On diminution of λ, the slit-width, and consequent

narrowing of the range of the exciting rays, the fluorescent spectrum is much weakened, but for λ = width of a sodium line, there is a species of scintillation, bright lines appearing and disappearing in succession in different parts of the spectrum.

The simple re-emission, when there is actually intensification of the brilliancy of the rays, as for the principal sodium line, Wood considers to be a resonance effect pure and simple, and to be distinguished from the fluorescence proper.

§ 154. Fluorescence in General.

Although we have now good reason to suspect that similar transformations not limited to the visible spectrum are capable of being effected by matter absorbing light, yet fluorescence was historically limited to transformations in which the re-emitted light was confined to the visible spectrum, the distribution of energy being, however, modified. The similarity in some respects of the phenomena with those of the scattering of light in turbid media caused Brewster to term it internal dispersion, and Herschel[1] epi-polic dispersion.

§ 155. Stokes' Law and the Redistribution of Energy.

Stokes laid the foundations of accurate and critical analysis of fluorescent phenomena in a magnificent series of papers commencing in 1852,[2] and although some of his deductions have required modification, the methods of investigation he introduced and the distinctions which he drew attention to have formed the solid core of all subsequent work on the problem.

If a beam of light be, on the wave-theory, supposed completely specified by its colour or finite range of vibration-frequencies, and its state of polarization, then the evident

[1] *Phil. Trans.*, 1854, p. 145.

[2] *Phil. Trans.*, [2] 143, 463 (1852). For a comprehensive review of the whole question see H. Kayser, *Handbuch d. Spectroscop.*, Bd. 4, 854 (1905).

phase-change which light undergoes in fluorescent media must be attributed to a change in one of these characteristics. Stokes concluded that no change in state of polarization fitted the phenomenon, and concluded that there must be occurring a transformation of invisible into visible vibrations. He distinguished fluorescence from scatter by the absence of polarization in the case of fluorescent light, and by the clarity of the fluorescent medium.

The means of discriminating fluorescence which he devised were twofold.

(*a*) Complementary colour-filters in the path of the beam.

Given two complementary colour-filters which together absorb the whole spectrum, then this opacity will be unaffected if a non-fluorescent substance is placed between and a beam passed through one filter. If, however, the first filter, nearest the source, let through rays capable of making the substance fluoresce (or conversely, if the substance fluoresce in the transmission-band of the first filter), then it will be perceived through the second filter. Stokes used combinations of cobalt and manganese glass, and of ammoniacal copper sulphate versus yellow (silver) glass, but many more combinations have been rendered possible by the evolution of the dye-industry and the utilization of colour-filters in photography.[1]

(*b*) Method of crossed prisms.

The fluorescent body is illuminated serially with quasi-monochromatic light from a solar prismatic spectrum, and a second prism is placed so as to deviate the ray from the fluorescer at right angles to its length. For substances following Stokes' law, the fluorescent spectrum does not extend as far as the primitive spectrum.

The validity of this law, to the effect that the wave-length of the fluorescent light was universally greater than that of the exciting ray, became the crux of polemic and investigation. It was contradicted, both on experimental and theoretical grounds, by Lommel,[2] but reconfirmed for a wide range of

[1] See *An Atlas of Absorption Spectra*, by C. E. K. Mees (Longmans, 1909).

[2] *Pogg. Ann.*, **160**, 75 (1877); *Wied. Ann.*, **3**, 113 (1878).

substances by Hagenbach.[1] A lively controversy arose as to whether so-called negative fluorescence existed, *i.e.* whether infra-red rays could give rise to visible or ultra-violet radiation.[2] Various results obtained by concentration of infra-red rays were interpreted in this sense. The generalized displacement principle of Wien and Planck (p. 60) on the equilibrium of radiation shows that as soon as a body of radiation is sufficiently coherent to be attributed a temperature in a thermodynamic sense, work of compression or condensation done upon it must increase the temperature and displace the optical centre of gravity toward the shorter wave-lengths. Hence arguments from the effect of concentrated infra-red rays may be considered to support "negative fluorescence" or not, according to the interpretation of the term. Once the occurrence of exceptions to Stokes' rule is admitted, then the question of the reversibility of fluorescence, as of other processes involving dissipation of energy, merges into the wider problem of possible processes, not contradictory of the practical onus of the second law of thermodynamics, but actually operative in a sense contrary to it, namely, in the sense of concentration of energy, other than those vitally and purposefully controlled to that end. Actually, the chief difficulty in testing Stokes' rule lies in the accompaniment of scattered light, which like a blare of undesired sound enveloping a melody, drowns the motif. However, careful experiments by Stenger[3] and by Stenger and Hagenbach together established the real existence of a large number of exceptions to the rule beyond doubt, and this very restricted validity has been since confirmed by Nichols and Merritt. In fact, if spectrophotometric determinations had been made instead of eye-estimates, it is possible that the rule would never have been framed. Stenger used a narrow strip cut out of a pure spectrum, and showed that with nearly all cases, light of wave-length greater than that of the fluorescent band

[1] *Pogg. Ann.*, **146**, 65, 508 (1872).
[2] See H. Kayser, *Handbuch d. Spectroscop.*, Bd. 4, p. 863.
[3] *Wied. Ann.*, **28**, 201 (1886).

could excite it. This was especially evident with eosin and fluoresceïn.[1]

Stenger concluded :—

(*a*) Every maximum in the absorption spectrum of the fluorescer is correlated to a maximum at approximately the same position in the fluorescent spectrum, but the intensity-gradient in the fluorescent spectrum is much flattened.

(*b*) With increased concentration of the fluorescer, the intensity of fluorescent light first increases, reaches a maximum, and then decreases again. This law of an optimum concentration was found by Stokes.

(*c*) The ratio of the fluorescence from a superficial layer to that from an interior layer increases with the absorption, but becomes less the greater the observing distance.

Wood has shown that fluorescing bodies do not in general follow Lambert's law, the intrinsic brightness increasing with oblique observation.

Later researches by Nichols and Merritt[2] and Wick,[3] show that different fluorescing substances exhibit many anomalies, difficult to bring within the scope of any simple mathematical law. The results of the former observers as to relation of energy-distribution in the exciting light to the energy-distribution in the fluorescent light, for a solution of an eosine dye-stuff, are illustrated in the diagram. The curve convex to the x-axis shows the energy-distribution of the transmission band of the solution ; the curve concave thereto that of the fluorescent light. The broken curves are for a more concentrated solution.

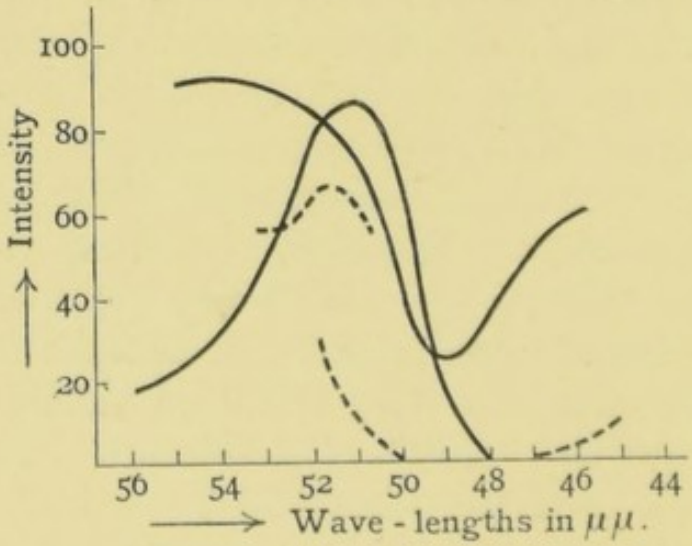


FIG. 46.

[1] *Wied. Ann.*, **33**, 577 (1888).
[2] *Phys. Rev.*, **18**, 412 (1904).
[3] *Ibid.*, **24**, 371 (1907).

They show that the fluorescence maximum does not coincide exactly with the absorption maximum, the fluorescence spectrum being displaced somewhat toward the less refrangible end of the absorption spectrum. But change of concentration, although leaving the general aspect of the distribution the same, modifies the ratios to some extent, the maximum being also slightly shifted toward the red.

From the intimate connection between absorption and fluorescence, it may be said that the general influence of solvents upon the fluorescence of bodies dissolved in them is much the same as their influence upon absorption (see p. 151). Typical of the relations between the spectrum of the light actually stimulating the fluorescer and the fluorescing spectrum is the following table from Nichols and Merritt :—

TABLE XXXVII.

Substance.	Fluorescence maxim.	Longest waves exciting fluorescence.
Fluoresceine . . .	517 $\mu\mu$	542 $\mu\mu$
Eosine	580 $\mu\mu$	589 $\mu\mu$
Naphthalene red . .	594 $\mu\mu$	589 $\mu\mu$
Rhodamine	554 $\mu\mu$	602 $\mu\mu$
Chlorophyll . . .	717 $\mu\mu$	720 $\mu\mu$
Quinine sulphate . .	437 $\mu\mu$	420 $\mu\mu$

In each case the fluorescence consisted of one band lying about the minimum of the absorption spectrum. The actual fluorescence is very remotely connected with the nature of the exciting light, but is rather an immediate function of the constitution of the fluorescing body. This leads us to consider the influence of chemical constitution and composition upon fluorescence.

§ 156. Relations of Fluorescence to Aggregation State and to Chemical Constitution.

T. S. Elston[1] has observed the fluorescent light from certain organic vapours when appropriately excited, in particular, anthracene (which we have already seen in photo-sensitive), and concludes—

(*a*) The spectra of vapours are similar to those of solutions.

(*b*) All rays in the absorption-band of a substance are capable of exciting fluorescence.

(*c*) The presence of certain gases does not affect the phenomenon, whilst certain others may increase the fluorescence, others diminish it.

(*d*) Increase of pressure diminishes the fluorescence, relatively considered. Here again the compromise between absorption and emission, as observed for concentration of solutions, comes into play, to give rise to an optimum pressure.

These experiments again point to the close connection between the "momentary bands" of phosphorescent bodies and fluorescence. It appears evident that, on the whole, solid solutions of certain "luminophores" or photo-sensitive groups of atoms, favour persistent bands, whilst liquid and gas solutions of the same luminophores favour the impermanent momentary bands, when the luminophores are excited by radiant energy. But it appears highly probable that the same groups of atoms, with a slightly varied kinematic grouping in the two cases (of momentary bands and persistent bands), are ultimately responsible for the characteristic peculiarities both of fluorescent and phosphorescent spectra. Also there is reason to believe that, alike for inorganic and organic substances, the modes of grouping of the atoms are essentially similar. But before advancing to the question of the relation of chemical structure to fluorescence, we may note some further facts connected with the absorption of light in fluorescent solutions which point to the actual grouping

[1] *Eder's Jahrbuch f. Phot.*, 1910, p. 310. Cf. also E. Ebert, *Wied. Ann.*, **53**, 144, and A. de Hemptinne, *Zeit. phys. Chem.*, **23**, 483 (1897).

proper to the fluorophore being to a considerable extent conditioned by the light incident, always provided that absorption is possible, so that fluorescence of some form may be said to be a usual concomitant of photo-chemical change, but generally in such cases the chemical change is virtual or isodynamic. The absorption of light in fluorescing systems is marked by certain singularities, which are, however, not dissimilar to those usually characterizing systems in course of photo-chemical change. Measurements of the absorption of light by fluorescing solutions have been made, *inter alia*, by Walter,[1] Knoblauch,[2] Nichols and Merritt,[3] F. Wick,[4] Burke,[5] and Camichel.[6]

§ 157. Fluorescence and Chemical Constitution of Bodies.

The preceding sections have dealt with fluorescence and phosphorescence from a kinetic point of view, as the general sign of certain partially reversible or virtual chemical changes involving alterations of valency-relations of residual affinity, but not necessarily final, being rather manifestations of the mobility of affinity within the closed circuits of certain definitely constituted groups of atoms. When the question is attacked from this point of view, and the correlation between fluorescence and chemical constitution investigated systematically, it is found that a very similar state of affairs obtains as is noted for selective absorption and chemical constitution. This is, in view of the dynamic connection of absorption and emission functions, only what we should anticipate, but the first to systematically trace the correlation of fluorescence with definite chemical constitutions was R. Meyer,[7] who worked with organic substances. He concluded that certain nuclei,

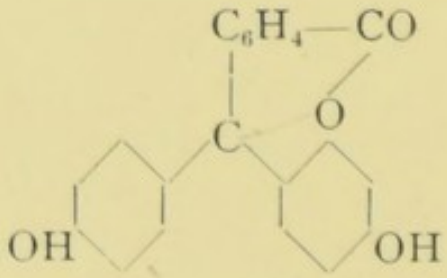
[1] *Wied. Ann.*, **36**, 502 (1889) ; **45**, 189 (1892).
[2] *Ibid.*, **54**, 193 (1895).
[3] *Phys. Rev.*, **24**, 356 (1907).
[4] *Jahrb. d. Radioaktivität*, **2**, 149 (1905).
[5] *Phil. Trans.*, **191**, 87 (1898).
[6] *Journ. de Phys.*, **4**, 873 (1905).
[7] *Zeit. phys. Chem.*, **24**, 268 (1897).

residues of radicles, which he termed "fluorogens," were invariably associated with the production of fluorescence. These groups are similar to the chromogens in the theory of dye-stuffs. Although a necessary condition of fluorescence, their existence alone is not a sufficient reason for actual fluorescence. For this it is essential that these nuclei, which are principally hetero-cyclic rings, should be in a state to enter into transient oscillatory interaction with certain contingent groups, which may be compared to the auxochromes (as auxo-fluors) of Kauffmann's theory.[1] It is not the static configuration which is responsible for the fluorescence, but the essence of the phenomenon is that certain configurations should be dissociated by an external force which they pass on in thus dissociating, and then be reconstituted, re-associated. It is the reclosing of the circuit which is marked or signalized by the extra-current of fluorescence, and the then kinematic *grouping* which is the actual fluorophore. As in colour, single-membered rings alone give no visible fluorescence, but rather a closed conjunction of such rings. For example, pyrone is non-fluorescent, as is also phenolphthalein.

Pyrone

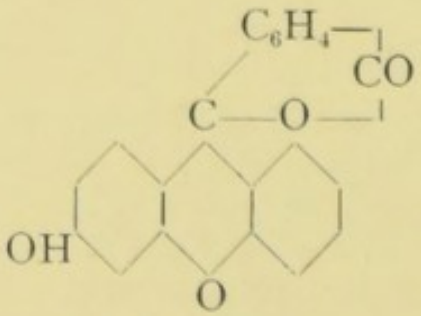
non-fluorescent

Phenolphthalein



non-fluorescent

Fluoresceïn

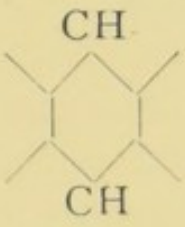


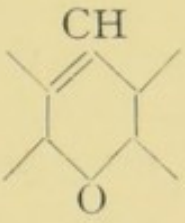
fluorescent

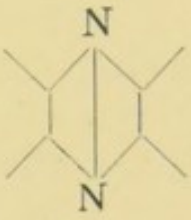
[1] See p. 169.

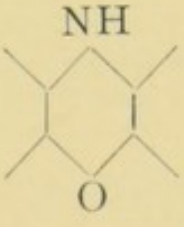
Substitution of negative elements, such as chlorine, may lessen the fluorescence, but this effect of substitution is again mitigated by the nature of the solvent. The action of this is at least as indeterminate as in the case of colour-production, there appearing to be all grades between mechanical indifference and true chemical combination. But definite selective fluorescence, as definite selective absorption, is undoubtedly due to the recurrent formation of identical definite chemical combinations. Amongst fluorescent groups of dye-stuffs, with the fluorogenic ring indicated, we may note—

Acridines fluorogen

Anthracene dyes  fluorogen

Xanthenes  fluorogen

Phenazines  fluorogen

Phenexazine  fluorogen

and similar thio-rings. It is important to notice that the invariant factor in a fluorophore is the fluorogen; the actual fluorophore itself may have a partially indeterminate constitution, being indeed a dynamic intermediate condition

which is only formed to be transformed in the transmission of more light.

Later, in conjunction with J. Stark,[1] Meyer finds that certain simpler phenols and aromatic residues, including benzene, show ultra-violet fluorescence, so that, as in the case of selective absorption, the benzene ring may be taken as one point of departure in the phenomena of fluorescence, which, on this ground, is not to be referred only to hetero-cyclic combinations.

The correlation of fluorescence with dynamic isomerism has been reviewed by Hewitt,[2] whilst Kauffmann has exposed his views on the matter in a separate monograph.[3]

§ 158. Fluorescence, Catalysis, and Biochemical Change.

The production of fluorescence is remarkably dependent upon small traces of subsidiary substances, of which, as in the case of phosphorescence, certain metals seem to be of principal importance, though many electrolytes are capable of affecting the phenomenon. Conversely, fluorescent substances are capable in the presence of light of greatly modifying the chemical metabolism in living tissues, which, in its most general aspect, may be said to consist in an electrolytic regulation of the formation of colloid structures. A series of researches on what he terms the "photodynamic action" of fluorescing dye-stuffs has been made by Tappeiner[4] and his co-workers. Experiments upon the combined action of light

[1] *Ber.*, **31**, 510 (1898); *Phys. Zeit.*, **8**, 250 (1907).

[2] *Brit. Ass. Ref.*, pp. 628-630 (1903).

[3] "Fluoreeszenz und Chemische Konstitution," *Ahrens Samm.*, Bd. 11 (Stuttgart, F. Enke, 1906).

[4] A. Iodlbauer and H. von Tappeiner, *Arch. klin. Med.*, p. 85 (1904); also "Ges. Untersuchung. uber d. photodynam. Erschein." (Leipzig, 1907); "Action on Ferments and Toxins," H. von Tappeiner, *Ber.*, p. 3035 (1903); and "Photodynamic Action on Yeasts and Yeast-sap (Zymase)," F. Locher, *Inaug. Dissert.* (Bonn, 1906); "On Protoplasm," H. Downes and F. P. Blunt., *Proc. Roy. Soc.*, **28**, 205 (1879); "Sunlight and Enzymes," O. Emmerling, *Ber.*, **34**, 3811 (1901).

and fluorescent bodies upon the activity of micro-organisms, enzymes, and other phases of vital change, showed—

(*a*) The activity of enzymes and toxins is inhibited by fluorescent substances in light, but not in darkness.

(*b*) Certain organic autoxidations, as of iodides, are accelerated.

(*c*) The photodynamic reaction on the protoplasm or ferment is not proportional to the apparent fluorescent light, but increases as this diminishes, provided it does not fall below a certain minimum. In this connection, the direct photo-sensitiveness of ferments, such as invertase, catalase, etc.,[1] to ultra-violet light, is worthy of remark, as well as the capacity of light to bring about organic reactions otherwise only induced by ferments.

As preliminary to the correlation of fluorescence with vital activity, we may notice that many of the fluorescing dye-stuffs form various grades of solution, ranging from suspensions through colloid solutions to true solutions, and that condensation of the true solutions to colloids may be effected by light, whilst conversely a dye-stuff giving no fluorescence, but a turbid solution in one solvent, can be made to give a true solution exhibiting fluorescence by modifying the solvent.[2]

§ 159. Fluorescence and Photo-chemical Extinction.

Wien, from the principle of harmonic displacement[3] of the optical and thermal centres of gravity of a limited body of radiation upon variation was led to the conclusion that a new absorption band should be formed in a substance which fluoresced in light. Burke,[4] from experiments with fluorescing uranium-glass, concluded that this was the case, and that a body fluorescing had a greater absorption than if not

[1] Cf. *Introduction to Bacteriological and Enzyme Chemistry*, G. J. Fowler (London, E. Arnold, 1911).

[2] See L. Michaelis, *Virchow's Archiv.*, 179, 195 (1905); S. E. Sheppard, *Proc. Roy. Soc.*, A. **82**, 256 (1909).

[3] "Temperature and Entropy of Radiation," *Wied. Ann.*, **52**, 132 (1894).

[4] *Phil. Trans.*, **191**, 87 (1898).

fluorescent. This may be stated differently, in the form, that whereas the absorption constant of non-fluorescent bodies is considered to be independent of the *intensity* of the light-source, this would not, following Wien's principle through, be true for fluorescent bodies, but for these the absorption should be a function of the *intensity* of the light. Now, much of the uncertainty in settling this and kindred problems [1] arises from the practical difficulty, which there are also theoretical reasons for supposing only approximately surmountable, of altering the *intensity* of light without altering its *quality*.

Burke's conclusions were traversed by Camichel, but supported by Nichols and Merritt, from experiments with aqueous and alcoholic solutions of eosin and fluoresceïn. They measured the transmission-curve of the solution for an acetylene beam, also the fluorescence excited thereby, and finally the total effect. Suppose now that T^{-1} be the absorption for light of wave-length, and F^{-1} the reciprocal fluorescence. Then if there is no alteration of the absorption, or reciprocally, of the transmission by fluorescence, we should have for the total effect $C = T^{-1} + F^{-1}$. Nichols and Merritt found experimentally that there was a small but constant difference, pointing to an increased absorption when fluorescence occurred.

Experiments with the light-source at different distances showed that the fluorescence-absorption increased with diminution of the distance up to a certain value, when a species of saturation seemed to set in. It is of course possible that this may be due to the varying absorption of the intervening medium for ultra-violet rays. The subject requires more experiment and also a consensus of opinion upon the interpretation of the data, for the problem is so beset with subjective elements that, as whenever the relation of subjective brightness of light to objective intensity is under discussion, one may say of it as W. K. Clifford did of a more general

[1] As, for instance, the determination of the range of validity of the Bunsen-Roscoe reciprocity-law for time and intensity in photo-chemical change.

thesis, "The question is one in which it is peculiarly difficult to make out what another man means, and even what one means one's self."[1]

§ 160. Mechanical and Electro-magnetic Theories.

Stokes, and more explicitly Lommel,[2] formulated theories to explain the phenomena of fluorescence on the wave-theory of light and the molecular theory of matter similar to those already noted in dealing with selective absorption and dispersion of light. These theories postulate the existence of molecules or atoms in the fluorescing substance capable of executing periodic vibrations syntonic with certain in the incident light, and in fact re-emitting light of the vibration-frequencies that they respond to. As the origin of the quasi-continuous fluorescent-spectra, they both suggested a strongly damped fundamental vibration, analyzing to a Fourier series of sine terms with diminishing amplitudes. Taking one species of molecule as responsible for one characteristic band, Lommel sets the displacement of the same from its original equilibrium as

$$F \sin ht$$

where F is a proportionality-constant depending on the light, h the phase, and t the time, for each wave-length effective. This displacement is further damped by a friction-term varying as the velocity and the force of restitution, a term responsible for the fluorescence; when developed to the second power of the displacement the integral contains both the free, the forced, and the upper partial derivatives of the fundamental vibration. The friction-term agrees with a dependence of the absorption upon intensity of the incident light, whilst also ensuring that the frequency of the proper period emitted is less than that of the period of strongest resonance, that is, of maximum absorption, which agrees with the relative displacement of the fluorescent band compared with the

[1] *Lectures and Essays*, **2**, p. 88; cf. R. W. Wood, *Phil. Mag.*, [6] **16**, 940 (1909).

[2] *Wied. Ann.*, **56**, 741 (1895).

absorption band, and the existence of fluorescent bands of finite amplitude.

Lommel's theory has been much modified and criticized since its genesis,[1] and the tendency has been either to abandon the attempt at an explicit molecular-mechanical image of the process, in favour of a purely statistical correlation of the facts, or to differentiate the molecular-mechanical theory yet more minutely in some application of the electron hypothesis. Attempts to discover the harmonics of the fundamental vibration, in the ultra-violet and infra-red regions, which are predicated on Lommel's theory, have led to no positive results, although the notion of ultra-violet and other invisible fluorescent bands has been promulgated.

Wiedeman and Schmidt[2] abandoned the attempt to formulate a definite molecular-mechanical image in favour of the physico-chemical theory of a complex molecule or molecular complex capable of pulsating iso-dynamically, this being mathematically expressible by a characteristic function, its "luminiferous receptivity." Assuming a reversible reaction of the type

$$\rightarrow \text{light} + \text{A} \rightleftharpoons \text{B}$$
$$\text{B} \rightleftharpoons \text{A} + \text{light} \rightarrow$$

then the re-emission of light is referred to the restitution of the molecule or particle to its initial state A, the molecule having, in consequence of this pulsation, at any moment, as possessing a dual personality, or rather, to be etymologically exact, dual translucency, two different refractivities, and correspondingly, two different absorption or extinction coefficients for light of wave-length within the range of periodicity of its own fundamental pulsation, and of which one value will, at any given moment in a given plane, be real, the other imaginary. Wiedeman's theory obviously links on to the notion of tautomery and dynamic isomery in chemistry, as conditioning fluorescence (see p. 176) his complex molecules with a definite "light-receptivity" approximating to the luminophores of

[1] See H. Kayser, *Handbuch d. Spectroscop.*, Bd. 4, p. 1988.

[2] *Ibid.*, *loc. cit.*

Kauffmann. Nichols and Merritt, whilst considering that the change of conductivity they observed in fluorescent solutions exposed to light indicated some form of electrolytic dissociation as concomitant therewith, suggested that this must be rather of the type effected by X-rays, etc., in gases, than that deduced as happening with simple electrolytes in aqueous solutions. The increase of conductivity which they found in fluorescent solutions on exposure to light has already been noticed (p. 374). Voigt has applied the ionization theory to the phenomenon. He considers as fundamentally characteristic of fluorescence :—

(*a*) The vibrations are free, only partially coherent ones, that is, their phase is only very slightly related to that of the exciting rays.

(*b*) All circumstances increasing or diminishing the number of free ions affect the magnitude of the fluorescence effect similarly.

(*c*) The fluorescent vibrations are only slightly damped. This aspect of the question cannot, however, be resolved without considering the interrelation of fluorescence and phosphorescence, and the damping or extinguishing influence of infra-red rays (see p. 403). Reference should also be made to Einstein's treatment of the subject.[1]

§ 161. Fluorescence and Radio-activity.

It is also worth noticing that the phenomena of fluorescence exhibit, in so far as the quantitative laws of increase and decay are concerned, considerable analogy with those of induced radio-activity, such as is exhibited by metals, etc., exposed to β-rays and Röntgen rays,[2] and indeed the sections on photo-electric currents show that there is reason to associate the phenomena causally.

In conclusion, we may notice a certain number of photo-echnic or catatypic actions in which the indicating apparatus was either a photographic plate or an electroscope, and which

[1] *Drude's Ann.*, **37**, 132 (1905).

[2] Cf. H. W. Schmidt, "On the Absorption and Scatter (Irradiation) of β-rays by Matter," *Ann. Phys.*, [4] **23**, 671 (1907).

have been adduced in support of the view that not only are all chemical reactions concomitant with a certain extrusion of electric radiations, but that radio-activity, such as is pre-eminently observed with radium, actinium, etc., is a special manifestation of a universal intra-atomic energy. All these actions consist either in the positive fogging of unexposed plates, or in the reduction of the fog or density of plates already exposed, the action of the substances in question being suspended by thin interleaves of some, but not of other, substances. References are given to certain papers, but it is hardly possible at this stage to effect any profitable analysis of the literature on the subject, although the observer overhauling the facts may perhaps extract something of value.

[1] See J. M. Eder, *Handbuch d. Phot.*, Bd. 1, p. 479 (1904). "Photo-echnic Action of Boron, Magnesium, and Lithium Nitrides," A. Remalé, *Ber. deutsch. Phys. Ges.*, **6**, 804 (1908); "Reaction-radiations," H. W. Woudstra, *Chem. Wk. blad.*, **5**, 835 (1908); K. Hof and H. Hahn ("Radiation from Mercury Compounds"), *Zeit. phys. Chem.*, **60**, 367 (1904); "Metal Emanations," L. Vazetti, *Atti R. Acad. Linc.*, [5] 171 (1908); Kahlbaum, *Phys. Zeit.*, **6**, 53; "Radiation from H_2O_2," J. Precht, and Otzuki, *Ber.*, **3**, 53 (1908); "Metals," E. Legrady, *Zeit. wiss. Phot.*, **6**, 60 (1908).

CHAPTER XI

ORGANIC PHOTO-SYNTHESIS

§ 162. Photolysis of Dye-stuffs.

Our last section must lead up to the central point in photo-chemistry, and the one which is still the least understood, viz. the photo-synthesis of food-stuffs by the chlorophyll function of green plants. This problem may be provisionally divided into two aspects: (*a*) the determination of the nature and chemical constitution of the chlorophyll group of pigments, and the manner of their derivation from proteins of the vegetable protoplasm; (*b*) the kinetics of the assimilation process, both in regard to the preliminary semi-mechanical absorption and adsorption of carbon dioxide into the leaf, and the fixation of CO_2 and H_2O to starches.

Before briefly touching on this all-important act of assimilation, we may devote a little space to a consideration of the action of light upon synthetic dye-stuffs, both in bleaching-out such dye-stuffs, and in forming them, under appropriate conditions from leuco-bodies.

Any given dye-stuff, exposed in a dispersed condition to white light, may—

(*a*) Retain its colour, shade, and vividity, over sufficient time to be termed fast.

(*b*) The colour may degrade or darken.

(*c*) The colour may bleach or lighten.

The stability of the dye-stuff is evidently a function of the intensity-gradient or energy-distribution of the light, that is, a function correlating intensity with wave-length or frequency.

As already pointed out (p. 168), the colour exhibited by the synthetic dye-stuffs depends upon selective absorption.

This absorption involves a certain oscillation or pulsation in the complex molecule of the dye-stuff, into the nature of which we need not enter here, beyond pointing out that in the case of fast or permanent dye-stuffs any physico-chemical change of state and constitution thereby involved must remain virtual, otherwise the dye-stuff will be impermanent. The art of desensitizing dye-stuffs so that they may remain fast to light, and which may in many cases be affected by the introduction of inhibitory elements or radicles into the complex molecules is too intimately part of the theory and practice of dye-making and dye-working to fall within the scope of this book. We can only deal briefly here with some of the factors involved in the reactivity of dye-stuffs in light, which have not only a mechanical importance in regard to their use in textile industries, but also a vital interest in the great part played by pigments and dye-stuffs in living matter.

It would be an error to suppose that the influence of light on colouring principles is only destructive, as in the well-known case of bleaching. It is equally capable of generating and deepening colour in suitable media. Thus the celebrated purple of the ancients was only brought to its full development when the preparation was brought into sunlight.

On such constructive and colour-engendering activities of light upon colour-bases we will speak briefly later; attention has already been drawn to this aspect of the question in dealing with chromatropy and colour-adaptation.

§ 163. Relation of Absorption to Change.

Whilst the energy taken in on selective absorption necessarily, on modern views, corresponds to the occurrence of a virtual or iso-dynamic reaction in the absorbing particles, this change is not sufficient of itself to imply any permanent after-effect. To ensure a complete, realizable reaction, a depolarizer is necessary. Hence the importance of the kind of solvent or substrate for the permanence or otherwise of dye-stuffs in light. Lazareff[1] has shown for certain dyes which bleach out

[1] *Drude's Ann.*, **24**, 661 (1907).

rapidly in white light, that by using "black" or temperature-radiation from a black body, hence light of known quality-value, the rate of decomposition was directly proportional to the energy absorbed per interval $\Delta\lambda$, and independent of the position of the absorption-maximum. He concluded that only a small fraction of the energy absorbed is spent in effecting the photo-chemical decomposition, the greater part being used up in heating the absorbing layer.

The chemical processes concerned in bleaching by light may be considered as primarily a reversible hydrolytic cleavage with irreversible autoxidation as a concomitant reaction. With respect to the upshot of the cleavage, and the nature of the colourless bleaching product, there has been considerable controversy. Whilst the majority of earlier observers[1] considered that the process was an oxidation, E. Vogel[2] referred it, in the case at least of the triphenyl-methane dyes with which he worked, to a reduction of these to the leuco-bodies, from which the dyes may be generated by oxidation. In support of this he found that fluoresceïn did not bleach out in the presence of H_2O_2, but did in a mixture of NH_2OH and KOH.

On the other hand, not only in the "mixed-black bleaching-out" process of colour-reproduction are peroxides used as sensitizers, but O. Gros[3] found in the bleaching of triphenyl-methane dyes that oxygen is used up. At the same time he noticed that many foreign additions could influence the change, in part catalytically, and also observed that the leuco-bases of these dyes are themselves light-sensitive to some extent.

Since then a great advance in the systematic investigation of the subject, as well as of the cognate problem of the relation of the photo-sensitiveness of dye-stuffs to their chemical constitution, has been made by K. Gebhard.[4] The results of previous observers might be summed up as follows :—

[1] On the history of the question see J. M. Eder, *Geschichte d. Photochemie u. Photographie* (Knapp, Halle, 1906); and K. Gebhard, *Uber die Einwirkung des Lichtes auf Farben* (H. Bauer, Marburg a. L. (1908)).

[2] *Wied. Ann.*, **43**, 449 (1891).

[3] *Zeit. phys. Chem.*, **37**, 157 (1901).

[4] *Uber die Einwirkung des Lichtes auf Farben* (Marburg a. L.,

(*a*) In bleaching by light, oxygen is used up and fixed.

(*b*) Water or water-vapour favours the reaction.

(*c*) Analytical impurities, particularly certain electrolytes and semi-electrolytes, influence the process.

Gebhard tested the point at issue between Vogel and Gros by comparing the action of arc-light for a five-day trial of six hours per diem upon pure tetraiodofluoresceine from Höchst, and an ordinary commercial specimen.

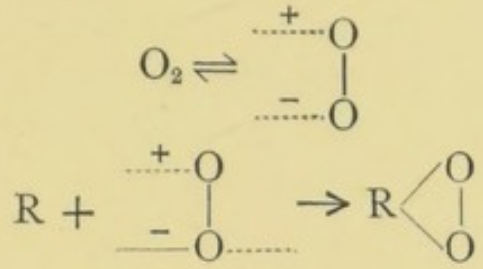
ACTION OF LIGHT.

Addition.	Höchst product.	Commercial product.
$NH_2OH + KOH$.	Darkened.	Lighter both in dark and light, but more so in light.
$KOH + H_2O_2$ . .	Little bleaching.	Little bleaching.
KOH	Bleaches both in dark and light, faster in light.	Bleaches rapidly.
H_2O_2	At first darkens, then bleaches.	Bleaches rapidly after darkening.

From these results, so opposed to Vogel's, it is concluded that though under rare conditions it may be possible photo-chemically to reduce dye-stuffs to the leuco-bases, which should then be capable of regeneration to the dye-stuff by a photo-chemical action of opposite sign, yet the dominant photo-chemical bleaching of dyes is an irreversible autoxidation process, the resultant product being quite different from a leuco-base, for it cannot be converted into the dye by oxidation. (In connection with this, the difference between the rapid and the persistent alterations in the chromatropic dye-stuffs (p. 341) should be compared, also the antagonistic action of rays of different period in so many photo-chemical changes.) The autoxidation itself may be either of the direct type, in that an unstable peroxide is first formed by the dye with activated

H. Bauer, 1908); *Zeit. angew. Chemie*, **22**, 433, 1890 (1909); and *Zeit. prakt. Chem.*, **84**, 561 (1911).

oxygen, which peroxide then breaks down to a lower, more stable one—



$$2RO_2 \rightleftharpoons 2RO + O_2$$

or another substance may act as an oxygen-carrier. The activation of the oxygen is conceivably favoured by the photo-electric currents which we have seen are given by many dye-stuffs, and which can thus autocatalytically hasten their own decomposition in light and oxygen.

The photo-chemical sensitiveness of dye-stuffs is to some extent associated with their capacity to act as optical sensitizers in conjunction with other sensitive materials, such as the gelatine-silver-halides of photographic plates. It depends in part upon the formation of a specific adsorption-complex of the dye with the substance sensitized. This photo-sensitizing is of considerable interest, as, apart from its importance in the practice of photography,[1] it suggests the line along which advance may be made in dealing with the problem of photo-synthesis.

We may also at this stage draw attention to the suggestive experiments made by Trautz[2] upon the *inhibition* or *retardation* of certain autoxidation-reactions effected by light of one colour (thermodynamically, quality-value) which *per contra* are *accelerated* by light of another hue, the reaction-mixture being kept in a thermostat. The reactions investigated were—

Autoxidation of pyrogallol, which is interesting as leading to naturally occurring colouring-matters.

Autoxidation of aqueous sodium sulphide.

Autoxidation of cuprous chloride, in hydrochloric acid or ammonia.

[1] The literature on colour-sensitizing is scattered through many technical journals. Good references may be found in J. M. Eder, *Handbuch d. Photog.*, Bd. 1 (Knapp, Halle, 1906). For a paper by C. Winther on "Colour-sensitizing of Eder's Solution," see *Zeit. wiss. Phot.*, 9, 205 (1911).

[2] Eder's *Jahrbuch d. Phot.*, p. 37 (1909).

The mixtures were not shaken or stirred during exposure.

Polar or antagonistic influence of red and violet light upon the reaction with Cu_2Cl_2 in ammonia was observed, the effect being measured by the pressure of oxygen over the solution. Pure sodium sulphide, free from sulphur or polysulphides, is practically insensitive to ordinary light; but colloid sulphur-nucleï and polysulphides, which colour the solution yellow, make it sensitive. Autoxidation is favoured by red light, inhibited by violet. In this, as in other cases, continuing or persistent actions after cessation of illumination were observed.

§ 164. Photo-sensitiveness and Constitution.

An important contribution to the correlation of photo-sensitiveness with chemical constitution of dye-stuffs has been made by K. Gephard.[1] He points out that not only must the relative nature and relative positions of substituents to one another and to the chromogen be taken into account in determining the stability or otherwise of a dye (and it hardly need be remarked that stability to light is the essential point here), but also the strength, distribution, and reactivity of the valencies or linkings between them. To express the sub-divisibility and reaction-capacity of the valencies, he adopts a modification of Thiele's theory of partial valencies[2] and the wavy line introduced by Bayer to express ionizable substituents in a complex. Thus a distinction is drawn between "ionization," as a reduction-division of the valency, and dissociation, implying complete segregation of the atoms. This is represented in the following symbolism :—

$$( )\ A{-}B \rightarrow \overset{\text{ionization}}{\sim\!A\!\sim\!B\!\sim}$$

$$( )\ A{-}B \rightarrow \overset{\text{dissociation}}{\overset{+}{A} + \overset{-}{B}}$$

the formula A—B, and the state of dissociation $\overset{+}{A} + \overset{-}{B}$, representing limiting conditions, antithetic states of the union of A and B, which is considered to be primarily ionized in

[1] *Journ. prakt. Chem.*, **84**, 561 (1911).

[2] Cf. J. N. Friend, *Valency*, this series.

the condition denoted by ~~~A~~~B~~~ by absorption of light. It is this quasi-desaturation of the doublets in any complex which affords the opportunity of adsorption to other bodies, either subsata or atmospheric gases. Gephard applies this conception to the elucidation of many particular phenomena in dye-stuff chemistry, for details of which the original paper should be consulted, and argues from it in support of the theory that in the dyeing of fabrics there is an inner chemical union between the dye-stuff and the fibre, not a mechanical adhesion merely. But in all cases of adhesion it is to be urged that the actual forces in operation do not differ intrinsically, but only in matter of interpretation, from chemical affinity. Although we cannot enter here into more detail on the photo-sensitiveness of dye-stuffs, it may be pointed out that the question is of considerable importance in more than one direction, and partly from the possibilty of its throwing some light on the problem of photo-synthesis, which is effected by chlorophyll. And at this point it may be suggested that, not only as Baeyer has indicated, do halogens and negative radicles play a prime part in the colour-disposition of organic dye-stuffs, but that, even in purified specimens, in which all metallic elements proper are supposed to be removed, it is not unlikely that traces of metals persist, the mutual energy of possible electrolytic couples determining in light to some extent the range of colour phenomena.

§ 165. Organic Syntheses in Light.

The efficiency of light in bringing about organic reactions, often only to be otherwise achieved by a very roundabout laboratory process, has frequently been remarked.[1] Of recent workers in this field we may notice in particular Ciamician and Silber,[2] H. Stobbe.[3]

Klinger[4] showed comparatively early that quinones could

[1] Cf. Gephard, *loc. cit.*, p. 565.

[2] *Ber.*, **36**, 4266 (1903), and many other papers; also in the *Atti Rom. Accad. Lincei*, **12**, 235 (1905).

[3] *Ber.*, **37**, 2232 (1904); *Ann. Chem.*, **349**, 333 (1906).

[4] *Ber.*, **31**, 1214 (1898).

be reduced in light to quinhydrones or ultimately to di-hydroxy-benzene under certain conditions, further that aromatic ketones underwent partial reduction and condensation to pinacone derivatives. Alcohols may also be oxidized up in stages similar to those effected by ferment-actions. An interesting reaction induced by light upon an alcoholic solution of nitro-benzaldehyde was observed by Ciamician and Silber.[1] The *m*-nitro-benzaldehyde exposed in absolute alcohol, as also the *p*-body, undergo slow transformation to resinous bodies. On the other hand, the *o*-body gives the ethylester of *o*-nitroso-benzoic acid. The sensitiveness of nitro-bodies has also been noticed by Sachs and Hilpert.[2]

In this connection the luminescence-accompaniment of several organic reactions deserve mention. Most of these involve autoxidation, in some cases apparently intra-molecular. Aldehydes, phenols, and alcohols in alcoholic solution give a strong luminescence with 30 per cent. H_2O_2, with bromine-water or other halogen in water. Examples are—

Acetylene (gaseous) with Cl_2 or Br_2 (gas) gives yellow-green luminescence.

Formaldehyde in alcoholic potash when shaken.

Carbazol, Anthracene, Phenanthrene, Anthraquinone — With bromine-water and hot alcoholic potash.

These reactions may perhaps yield some information on the processes occurring in luminous bacteria. A species of symbiosis, affecting the fixation of oxygen, appears to obtain between the leaves of certain plants and photogenic bacilli.[3]

§ 166. Photo-chemistry of Chlorophyll.

Chlorophyll or leaf-green is the name given to a heterogeneous aggregate of pigments extracted from plants; representatives also occur in certain animals, notably the Tunicata.[4]

[1] *Rendi. R. Accad. Lincei Rom.*, **10**, 228 (1901).

[2] *Ber.*, **37**, 186 (3425).

[3] H. Molisch., *Die Leuchtende Pflanzen u. Tiere* (Prag., 1902).

[4] This is still debateable, as the chlorophyll in certain of such cases appears to be due to a symbiosis of vegetable organisms (Algae) with

The heterogeneity of this aggregate, and the absence of any true chemical compound as the basis of chlorophyll, corresponds—

(*a*) To the prime function of chlorophyll as a photo-chemical sensitizer and ferment.

(*b*) To the nature of the aggregates as intermediate metabolic phases, maintained in very sensitive equilibrium by the reciprocal interaction of light and atmospheric forces on the one hand and the enzymes of the plant on the other.

Anything like a complete account of the work done on the physical and physiological side firstly of the assimilation question, and on the chemical aspect of the transaction secondarily, would take too much space. The principal investigations on the physical conditions of assimilation, the consideration of the energetics and economics of the process are due to C. Frémy, Timirazeff, P. Blackman, and Brown and Escombe. An excellent account of the influence of light upon plant-growth will be found in Pfeffer's *Physiology of Plants* (A. J. Ewart's translation), vol. ii. p. 85. Whilst Timirazeff has particularly studied the relation of assimilation to the energy-distribution in the light, and finds that the principal activity occurs in the yellow-orange-red, a minor action also being effected in the blue; he has also considered the variation of total intensity, and finds that the efficiency is very considerable for moderate intensities, but diminished greatly when the intensity is greatly increased. The curves illustrate the relative action in the spectrum. The ratio of fixation of carbon effected in the yellow to that in the blue is about 100 : 54.

The problem of the efficiency of the process has also been studied by H. T. Brown and Escombe.[1] A leaf, which may be still a member of its plant, is enclosed in a flat air-tight vessel with glass walls. A measured current of air is rapidly passed over it, and the amounts of CO_2 and H_2O determined subsequent to photolysis, a check experiment being performed without the leaf in a parallel vessel to determine the original

animal organisms; cf. *Plant-Animals*, F. Keeble, 1910 (Cambridge Manuals of Science).

[1] *Phil. Trans.*, **193**, B. 223 (1900).

proportions. The area of the leaf being measured, and the intensity of light and temperature altered at will, the efficiency

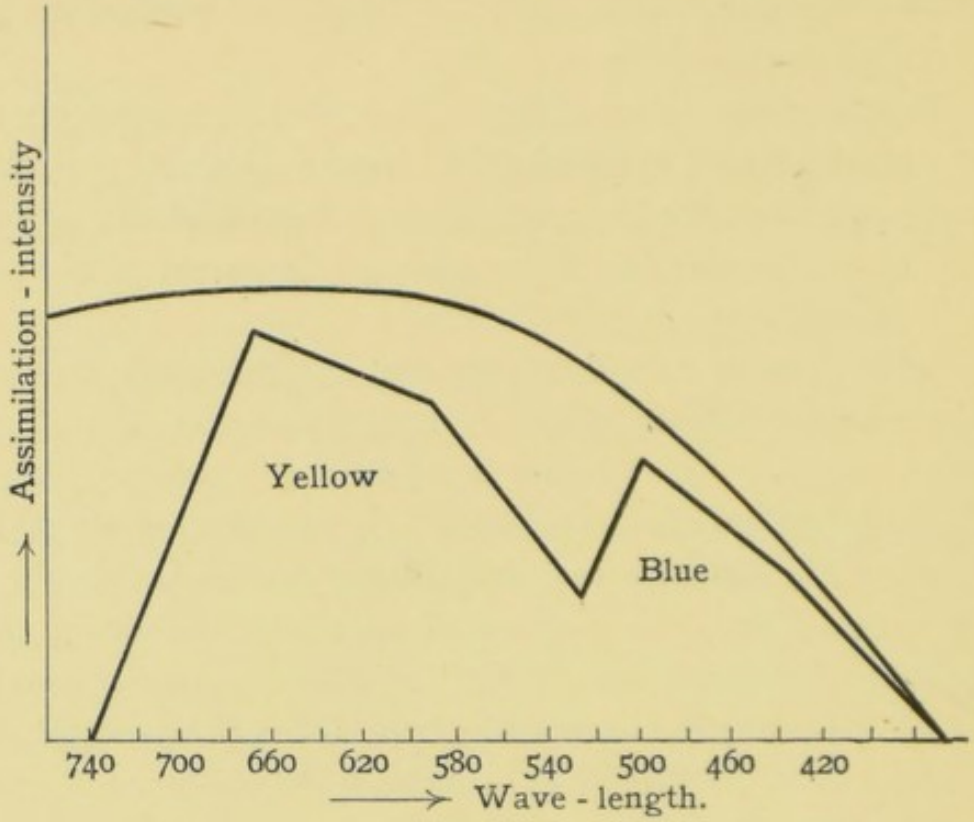


FIG. 47.

of the process can be estimated. The following table exhibits a typical set of results :—

TABLE XXXVIII.

Plant.	CO_2 absorbed per dm.² of leaf per hour.	Water transpired per dm.² of leaf per hour.	Energy in calories per cm.² leaf per minute.				
			Solar radiation falling on leaf.	Radiation absorbed by leaf.	Energy required for assimilation.	Energy required for transpiration.	Energy lost by irradiation and convection.
	c.c.	gms.					
Polygonum (June 19)	3·758	1·054	0·1942	0·1256	1·0031	0·1041	0·0184
Tropæolum (Sept. 4)	1·498	0·141	0·0889	0·0622	0·0012	0·0139	0·0471
Helianthus (Aug. 7)	2·134	1·259	0·2569	0·1762	0·0017	0·1243	0·0502

These experiments indicate a comparatively low efficiency in regard to the utilization of the incident radiation to

decompose CO_2, about 1·7 per cent. being the greatest percentage used. But very many other factors have to be taken into consideration, and the efficiency is not absolutely fixed, but varied to suit the economy of the plant.

§ 167. Mechanism of Assimilation.

As the experiments of Brown and Escombe have helped to demonstrate, the photolysis in the leaf cannot be considered apart from the atmolysis (diffusion-currents of the atmospheric gases) and the hydrolysis, or transpiration of water. These are consequent, and to some extent simultaneous processes with the photolysis proper, but if we consider them provisionally as independent, we may query the nature of the actual photo-synthesis. For all the low efficiency spoken of, relative to the gross leaf-area, if the microscopic anatomy of the leaf be taken into account, a somewhat different complexion is put upon the fact. Under optimum conditions the rate of absorption of CO_2 from air was found to be about one-half that of a 50 per cent. solution of caustic potash of equal area. Now the actual apertures between the guard-cells of the stomata, through which the gas must pass, do not form more than 1 per cent. of the total leaf-area, so that the actual rate of absorption of the CO_2 was some fifty (50) times as rapid as that into the potash. But we are yet in considerable ignorance of the process by which this influx is maintained. Empirically, the CO_2 is split into carbon and oxygen, which last is principally liberated as ordinary free oxygen. It is interesting to note that the atmosphere about a leaf is ionized, and we may recall at this point the decomposition of CO_2 which is effected by ultra-violet light and *Entladungstrahlen*. The main act of the fixation is the formation of carbohydrate

$$mC + mH_2O = C_mH_{2m}O_m$$

the suggestion being formerly that starch is the first carbohydrate formed (the production of which consequent with the photolysis may readily be shown with iodine), but the *starches* form a rather heterogeneous aggregate, of which the true starches (as distinct from inulin, etc.) have a six-membered

carbon-chain as unit, and all that we can be certain of so far as carbohydrate formation is concerned is that in consequence of the photolysis (which, in view of the fluorescence and luminescence of both the nitrogen-containing alkaloids, dye-stuffs, and proteins, as well as of the carbohydrates on iso-dynamic changes of state, is probably a true conduction of light, specific luminophores moving in the protoplasmic streams) a more or less determinate connectivity (*Vergliederung*) of carbon-atoms with attached side groups and chains is continually built up, breaking down locally to supply the more readily extractable and crystallizable components of the organism.

Baeyer suggested that formaldehyde, CH_2O, is first formed, according to the equation

$$CO_2 + H_2O = CH_2O + O_2$$

which is then condensed to a hexose

$$C_6H_{12}O_6$$

but the evidence in favour of this hypothesis is somewhat scanty. Priestley and Usher claim to have formed formaldehyde from CO_2 and water by "dead chlorophyll" from killed leaves, in the presence of sunlight and uranium.

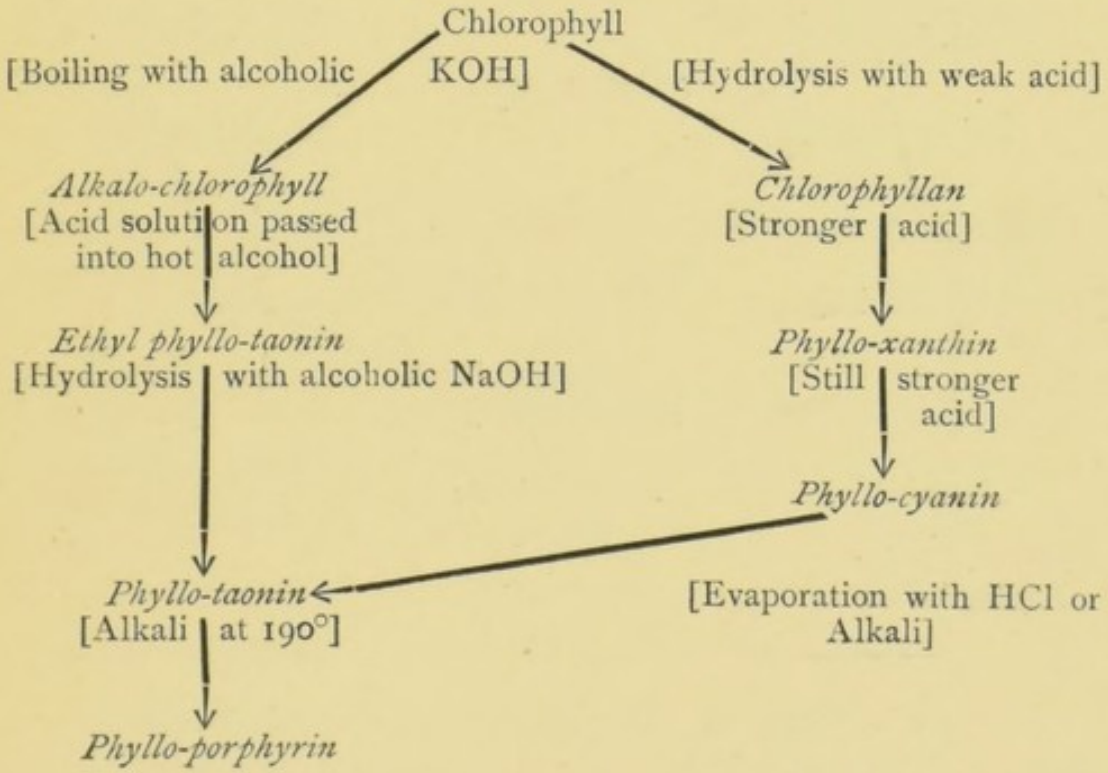
From Brown and Morris' investigations it appears highly probable that cane-sugar is the first sugar formed, from which diastases in the leaf rapidly form maltose, dextrose, levulose, and such readily soluble sugars which can easily undergo translocation in the sieve-tubes and be recondensed elsewhere if necessary to reserve food-stuffs.

§ 168. The Chemical Nature of Chlorophyll.

As already stated, this is rather an indeterminate group or aggregate of substances in flux than a definite chemical species. But it is possible to isolate a series of fairly definite products from the crude extracts with alcoholic solvents. In this process of fractionation the names of Hoppe-Seyler, Schuncke and Marchlewski, and Willstätter stand out particularly. By far the most important result of their labours is to show the very close affinity between the hæmoglobin-pigments of the

blood of animals and the chlorophyll group. Hoppe-Seyler obtained by alcoholic and ethereal extraction of grass leaves, a crystalloid substance, *chlorophyllan*, which gave upon decomposition with KOH an acid, *chromantinic acid*. This yielded with excess of mineral acid a purple-blue pigment, *phyllo-porphyrin*, the composition and properties of which are very similar to those of *hæmatoporphyrin*, obtainable from *hæmin* of the blood. The gist of Hoppe-Seyler's work is exhibited in the following table, taken from a review of the chlorophyll investigations by C. Schryver[1] :—

TABLE XXXIX.

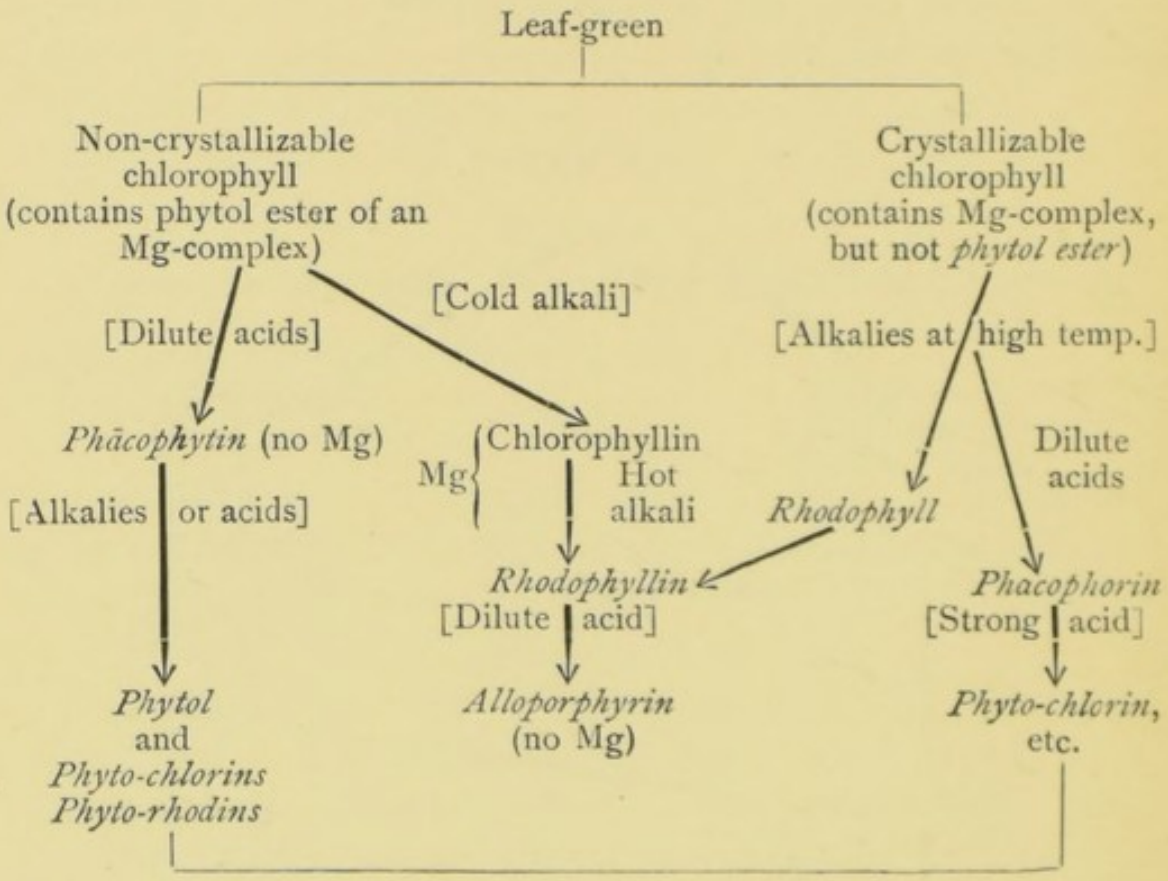


Willstätter and his co-workers, using a different series of purifying methods, obtained from the products of mild acidic or alkaline hydrolysis of *chlorophyll* substances, which on fractionation of their ethereal solutions with acid in graded strengths gave a new series of products, which he divided into two main groups, the *phytochlorins* (blue to green pigments) and the *phytorhodins* (reddish pigments). A fact of considerable importance educed by Willstätter is that magnesium is an

[1] *Sci. Prog.*, No. 11, p. 432 (1909).

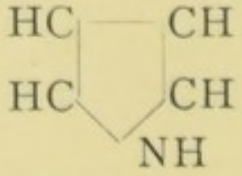
essential constituent of the chlorophyll group of activities, holding much the same position with regard to them that iron does in blood-pigments. Part at least of the chlorophyll aggregation is an ester of an unsaturated alcohol, termed *phytol* by Willstätter. The main steps of this investigation may be given as follows :—

TABLE XL.



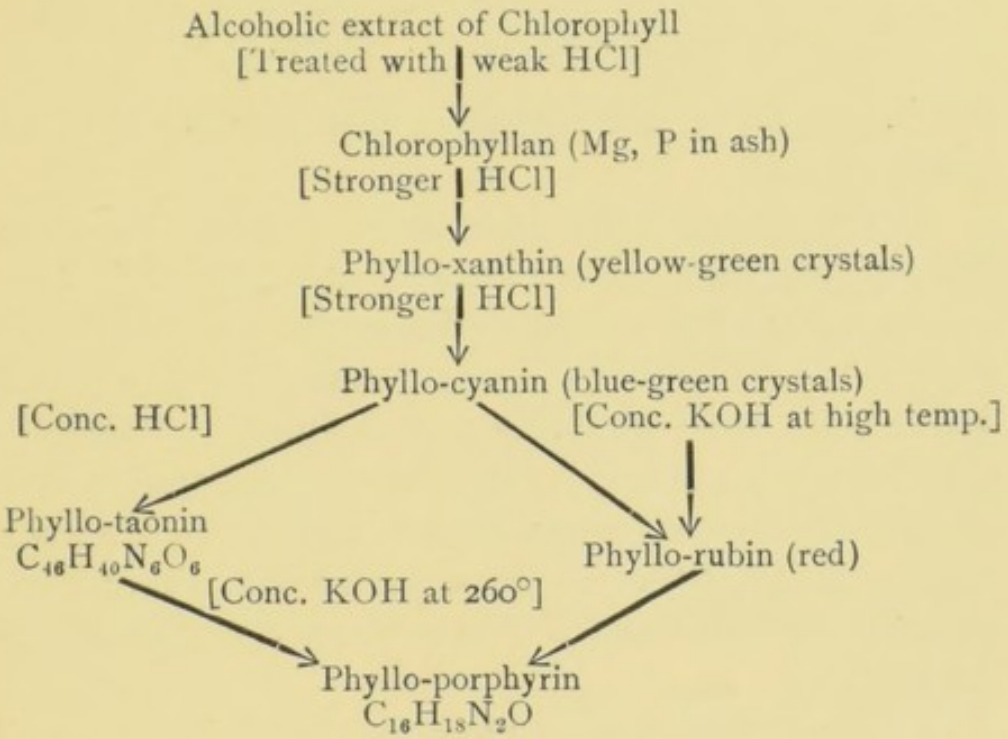
No doubt many of the pigments of the *phyto-rhodin* group are similar to the red and fulvous pigments common in most *leaves* towards autumn, but also occurring at any stage of the year in the other parts of plants.

The work of Schunck, Marchlewski, and Nencki is also of great importance in this direction ; they established the affinity of the chlorophyll pigments with heterocyclic ring compounds of a simpler type such as pyrrol—



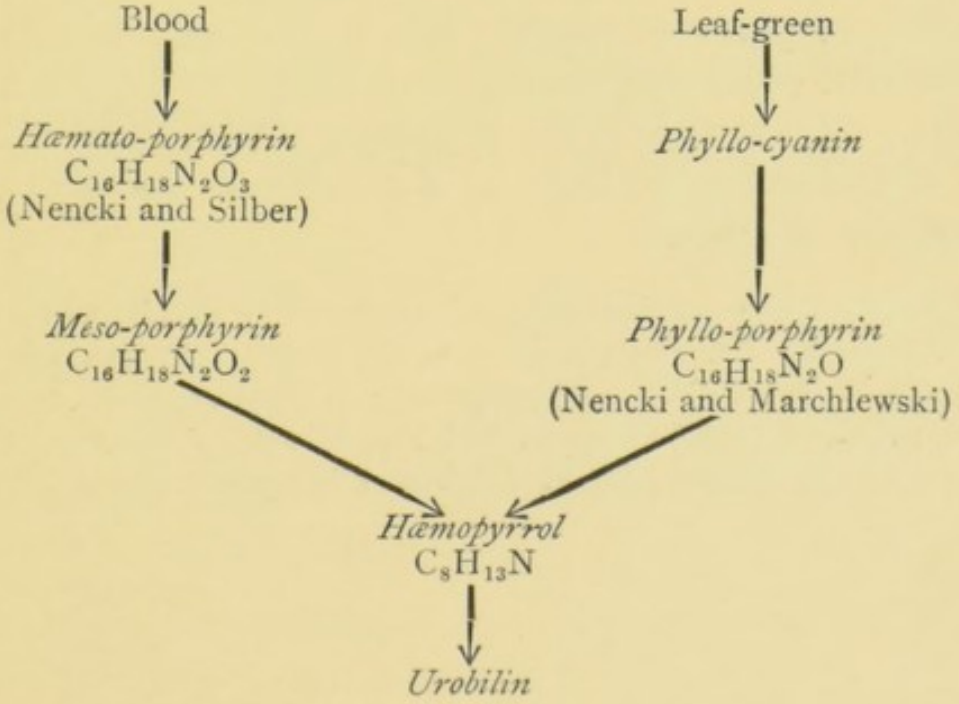
The principal operations and results of these investigators are shown in the following table :—

TABLE XLI.



It will be useful in this conjunction to give a brief comparison table of the reduction of derivatives of blood and leaf-green to a common body.

TABLE XLII.



The intimate relationship of the blood-pigment hæmato-porphyrin and the leaf-green pigment phyllo-porphyrin, is vouched for to some extent by the nearness of their empirical formulæ :—

Hæmato-porphyrin $C_{34}H_{35}O_6N_4$
Phyllo-porphyrin $C_{34}H_{38}O_2N_4$

By reduction of the former, a meso-porphyrin, $C_{34}H_{38}O_4N_4$, was obtained.

Other pigments are also isolated from leaf-green beside chlorophyll, such as carotin and xanthophyll. True, these substances are yet almost as indeterminate in constitution as the protein-components of the plasmas from which they are derived, but the importance and magnitude of such investigations cannot be judged solely from the conformity or otherwise of any separate stages to certain rigid criteria of purity and singularity, but rather by the sequence and progression of steps by which the unknown is drawn within the expanding circle of the known.[1]

The heterogeneity of chlorophylls derived from different sources, the specific differences between the chlorophyll from one species of green plant and another, owes very little to adventitious or accidental causes, but is rather a direct continuation of the heterogeneity of the protoplasms of the different species in question. If, subjectively, sight has a hegemony as *primus inter pares* among the senses, the same may be said, objectively, of its medium, light, in regard to the energies of nature. We are only at the beginning of the conscious utilization of the powers of light, as distinct from the unconscious enjoyment of them.

[1] A very comprehensive review of the chemistry of chlorophyll is given by C. Schryver, *Sci. Prog.*, No. 11, p. 432 (1909). Further see Hoppe-Seyler, *Zeit. physiol Chem.*, **3**, 339 (1879) ; Willstätter, *Lieb. Ann.*, **350**, 1 (1906) ; *ibid.*, 48 (1906) ; Schunk and Marchlewski, *Lieb. Ann.*, **278**, 329 (1894) ; also H. Hansen, *Die Farbstoffe des Chlorophylls* (Darmstadt, 1889).

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