

A History of Chemistry
Jr. Partridge.

CHAPTER XXII

PHOTOCHEMISTRY

Johann Heinrich Schulze (Colbitz, Magdeburg, 12 May 1687–Halle, 10 October 1744), a pupil of Hoffmann at Halle (see Vol. II, p. 691), moistened chalk with a solution of silver in aqua fortis and found that on exposure to bright sunlight it became deep red, inclining to violet-blue, on the surface. The chalky mass was then partly dissolved in nitric acid, diluted with water, and poured into a tube, when the side of this exposed to sunlight became similarly coloured. No colour was produced on heating the tube before a fire. By pasting pieces of black paper on a bottle containing the suspension and exposing to sunlight, the sun's rays 'wrote on the chalky sediment' the words and sentences cut out of the paper by a knife.¹

J. B. Beccari and Bonzius² examined the fading of coloured ribbons in sunlight (violet faded first) even in air-tight vessels, whilst they did not fade (but lost brilliance) when heated in the dark (Bonzius). Freshly-precipitated silver chloride in a glass turned violet on the side exposed to light. If a strip of black paper was stuck on the exposed side of the glass, the part of the silver chloride behind it remained white (Beccari).

Bergman³ found that silver and mercurous oxalates blacken in sunlight. Scheele⁴ found that metallic silver is formed in silver chloride blackened by light, and that 'it grows black sooner in the violet than in any of the other rays', the first distinction of the different chemical effects of light of different colours. He seems to have known of Schulze's work.⁵

A. Hagemann, of Bremen,⁶ found that powdered guaiacum resin exposed to light in a barometer tube with exclusion of air became bright blue, but became grey when exposed to air. This was confirmed by J. Senebier,⁷ who mentions

¹ J. H. Schulze, *Scotophorus pro phosphoro inventus; seu experimentum curiosum de effectu radiarum solarium*, in *Acta Physico-Medica Academiae Caesareae Leopoldino-Carolinae Naturae Curiosorum exhibentia Ephemerides*, Nürnberg, 1727, i, 528–33 (other, medical, papers by Schulze in the same vol.); tr. by Litchfield, *Tom Wedgwood the First Photographer*, 1903, 217–27; Eder, *History of Photography*, tr. Epstean, New York, 1945, 56–83. Schulze must have known of the earlier (1722) experiment of his teacher Hoffmann (*Opera*, 1740, iv, 541); for other publications by Schulze see Bolton, (1), 821; Ferguson, ii, 348; his experiments are mentioned by Lewis, *Commercium Philosophico-Technicum*, 1763, ii, 350; and by Priestley, *History of . . . Vision, Light and Colours*, 1772, i, 379–80.

² *De Bononiensi Scientiarum et Artium Instituto atque Academia Commentarii*, Bologna, 1757, iv, 74–87; De vi, quam ipsa per se lux habet, non colores modo, sed etiam texturam rerum, salvis interdum coloribus, immutandi.

³ *De acido sacchari*, 1776; *Essays*, 1788, i, 323.

⁴ *Über Luft und Feuer*, 1777, §§ 63, 66; Guareschi, *Atti R. Accad. Torino*, 1914 xlix, 1083.

⁵ *Ib.*, § 60.

⁶ *Crell's N. Entdeck.*, 1782, iv, 61–7.

⁷ *Mémoires Physico-Chimiques, Sur l'influence de la lumière solaire pour modifier les êtres des trois règnes de la Nature, & sur-tout ceux du règne végétale*, 3 vols. 8°, Geneva, 1782, ii, 408; *Crell's N. Entdeck.*, 1782, vi, 147; 1783, xi, 211–26.

Schulze. He found the times in seconds required for light of different colours to discolour silver chloride: violet 15, purple 23, blue 29, green 37, yellow 330, orange 720, red 1200 (the last two did not give an intense colour).¹ He made experiments on the growth of vegetables in light of different colours,² supposing (erroneously) that violet light produces the green colour because it is more phlogisticated.³ He thought the green resino-extractive matter (chlorophyll) is a kind of 'vegetable Prussian blue' (like indigo), or a kind of soap.⁴ A solution of it in alcohol, ether, or essential oils, is bleached by sunlight but only in presence of air.⁵ Tinctures of flowers and various dyestuffs,⁶ coloured woods and ribbons,⁷ oil and water colours, dyed fabrics and papers,⁸ oils and essential oils,⁹ and yellow wax,¹⁰ are bleached by sunlight. Senebier regarded light as a phlogisticating body,¹¹ but not identical with phlogiston,¹² or with heat or electricity.¹³

Ritter¹⁴ found that moist silver chloride exposed to the solar spectrum darkens first in the invisible part beyond the violet; slightly darkened silver chloride becomes lighter in the red rays, and since this also occurs in light formed by mixing the red and violet ends of the spectrum, 'the reducing rays must be present to a far greater extent in white light than those which oxidise.' He thought the red end oxidised and the violet end reduced. This discovery of ultraviolet light was confirmed by Wollaston, who mentions Ritter.¹⁵ The infrared rays were discovered by Scheele (see Vol. III, p. 226) and investigated by Sir William Herschel.¹⁶

Thomas Johann Seebeck (Reval, 9 April 1770-Berlin, 10 December 1831) communicated some observations on the chemical action of the solar spectrum to Goethe, who incorporated them in an appendix to his *Geschichte der Farbenlehre* (1810).¹⁷ Seebeck found that if moist silver chloride is exposed to a solar spectrum, the part in the violet and a little beyond becomes reddish-brown tending to violet, the part in the blue becomes blue, becoming fainter in the green; in the yellow there is little or no action, in the red or infrared a rose colour resulted. Seebeck found that silver chloride turned grey under violet, blue, or blue-green glass; that the moist chloride which had turned grey in ordinary light became lighter in colour in yellow light; and that red oxide of mercury under blue glass is changed to grey by sunlight. He found that a mixture of hydrogen and chlorine in a dark blue glass combined rapidly, but without explosion, when exposed to sunlight, whilst in a yellowish-red vessel the action was very slow.¹⁸ In 1812 he found that the mixture exploded when exposed to the flame of a Bengal light.¹⁹ C. H. Pfaff could not

¹ *Ib.*, 1782, iii, 192 f., 199.

² *Ib.*, ii, 195 f., 207 f., 366 f.

³ *Ib.*, iii, 1-25.

⁴ *Ib.*, ii, 303 f., 336 f.

⁵ *Ib.*, iii, 169; *Ann. Chim.*, 1791, xi, 89 (action of oxygen).

⁶ *Obs. Phys.*, 1791, xxxviii, 56.

⁷ *Ib.*, iii, 205 f.

⁸ *Intelligenzblatt der Erlanger Literaturzeitung*, 1801, no. 16, 121-3 (22 February); *Ann. Phys.*, 1801, vii, 527 (7 lines); 1802, xii, 409-15.

⁹ *Phil. Trans.*, 1802, xcii, 365 (379); *Ann. Phys.*, 1811, xxxix, 291.

¹⁰ *Phil. Trans.*, 1800, xc, 255, 688, 692, 748.

¹¹ Goethe, *Werke*, ed. Kalischer, Hempel, Berlin, 1879, xxxvi, 431 (439-44).

¹² *J. Chem.*, 1811, ii, 263.

¹³ *Ib.*, ii, 59.

¹⁴ *Ib.*, ii, 354 f.; iii, 350.

¹⁵ *Ib.*, iii, 114 f., 134 f., 211 f.

¹⁶ *Ib.*, iii, 218 f.

¹⁷ *Op. cit.*, 1782, ii, 207, 366 f.

¹⁸ *Ib.*, 253 f.

¹⁹ *Op. cit.*, 1782, ii, 207, 366 f.

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confirm the spectrum experiment.¹ The action of light on silver chloride was investigated by N. W. Fischer.²

Wollaston found that guaiacum becomes green in the violet and blue rays but no effect was observed in the yellow, and the green material was restored to the original tint by the red rays, the action of which was due to heat. He proposed the name 'chemically active rays'³ instead of Ritter's name 'reducing rays', since guaiacum is oxidised, not reduced, by violet rays. E. Becquerel⁴ still spoke of 'rayons chimiques' and 'rayons phosphorogéniques'. He found that with an iodised silver plate the red, orange, and yellow rays have the quality of continuing the action of the more refrangible rays, and he called them 'rayons continuateurs'.⁵ Bérard⁶ distinguished calorific (infrared), colorific (visible), and chemical (violet and ultraviolet) rays, and said the chemical effects of light were not due to heat. Berthollet⁷ had distinguished the chemical effects of heat and light. Heinrich August Vogel (who was in Paris from 1802 to 1816) made experiments on the action of red and blue light on various substances.⁸

The first true photographs were made by Thomas Wedgwood (see Vol. III, p. 297), whose results were written up by Davy.⁹ White paper or white leather moistened with silver nitrate solution was not affected by red light; yellow and green light acted, but blue or violet light was more effective. The dried paper could be varnished, but it was not fixed. Wedgwood could not form images with a camera obscura but Davy obtained them with a solar microscope. Davy¹⁰ found that precipitated silver iodide is 'much more rapidly altered by exposure to light, than the muriate of silver [AgCl]', but this is true only if it is precipitated with silver nitrate in excess.¹¹

GROTTHUSS

John Robison¹² found about 1787 that silver nitrate is less blackened by sunlight passed through a bottle of nitric acid than by direct sunlight, and this was confirmed by C. W. G. Kastner.¹³ Richter¹⁴ recognised that in Scheele's experiment on the decomposition of nitric acid (see Vol. III, p. 226), the light must be *absorbed* (verschlucket).

Grotthuss,¹⁵ in a paper entitled 'Ueber die chemische Wirksamkeit des

¹ *Über Newton's Farbentheorie, Herrn von Goethe's Farbenlehre und den chemischen Gegensatz der Farben*, Leipzig, 1813; J. M. Eder, *History of Photography*, 1945, 155.

² *Über die Wirkung des Lichtes auf das Hornsilber*, Nürnberg, 1814; Lorenz and Höchberg, *A. Nat.*, 1913, iv, 323.

³ *Ann. Phys.*, 1811, xxxix, 291; D. Brewster, *A Treatise on Optics*, 1831, 91.

⁴ *Ann. Chim.*, 1843, ix, 257-322 (263).

⁵ *Compt. Rend.*, 1841, xiii, 198-200.

⁶ *Mém. Soc. Arcueil*, 1817, iii, 5-47; read to the Institut 21 December 1812.

⁷ *Statique Chimique*, 1803, i, 192.

⁸ *J. de Phys.*, 1813, lxxvi, 388-96; 1815, lxxx, 245-57; Ruhland, *J. Chem.*, 1813, ix, 236-9.

⁹ *Journals of the Royal Institution*, 1802, i, 171 (June); Davy, *Works*, 1839, ii, 240; R. B. Litchfield, *Tom Wedgwood the First Photographer*, 1903.

¹⁰ *Phil. Trans.*, 1814, civ, 74; *Works*, 1840, v, 440.

¹¹ R. Hunt, *Researches on Light*, 1854, 81.

¹² In Black, *Lectures on the Elements of Chemistry*, 1803, i, 534; see Scheele, Vol. III, p. 226.

¹³ *Repertorium für die Pharmacie*, Nürnberg, 1822, xiii, 44.

¹⁴ *Ueber die neun Gegenstände der Chemie*, 1793, iii, 98.

¹⁵ *Jahresverhandlungen der Curlandischen Gesellschaft für Literatur und Kunst*, 1819, i, 119 (124); *Ann. Phys.*, 1819, lxi, 50-74 (59); Ostwald's *Klassiker*, 1906, clii, 101, 104.

Lichtes und der Elektrizität', in which he compares the action of light with electrolysis, refers to some experiments by Davy¹ and says:

'Meiner Einsicht nach muss derjenige Körper, abgesehen von seiner chemischen Natur, am kräftigsten auf ein gegebenes farbiges Licht, und umgekehrt letzteres auf ihn, reagieren, der im natürlichen Zustande eine diesem farbigen Lichte *entgegengesetzte* Farbe zeigt.

Das farbige Licht diejenige Farbe der ihm ausgesetzten Körper zu zerstören sucht, die seiner eigenen *entgegengesetzt* ist, und dass es seine *eigene*, oder ihm *analoge* Farbe, darin zu *erhalten* strebt. Die chemische Wirkung muss daher im zusammengesetzten Verhältnis stehen mit der Veränderbarkeit der anzuwendenden Substanz und dem Gegensatz ihrer natürlichen Farbe.'

Grotthuss's statements are given in the originals, since they are claimed to have anticipated the law stated by Draper (1841, see p. 717) that only light which is *absorbed* by a substance can produce chemical action. Grotthuss assumed that a ray of light behaves as an alternation of positive and negative electricities, + - + - + - (an anticipation of the electromagnetic theory of light), and its chemical action is due to these. Robert Hunt² also suggested a 'peculiar electric action existing in the different rays of light'. Grotthuss criticised Ritter's theory³ that the prismatic spectrum is like a voltaic pile, the red ray being the oxidising pole (+) and the violet the deoxidising (-), since (said Grotthuss) each ray produces simultaneous oxidation and reduction. Ritter, and Winterl,⁴ correctly assumed that the combination of the two electricities produces heat, but, says Grotthuss, they proposed theories incapable of experimental verification. Grotthuss⁵ discovered the accelerating effect of light on oxidations by free oxygen.

DRAPER

John William Draper (St. Helens, Lancs., 5 May 1811—Hastings, U.S.A., 4 January 1882) studied chemistry in London University. In 1832 he emigrated to America. In 1836 he became M.D. of Pennsylvania and professor of chemistry and physics in Hampden-Sidney College, Virginia, in 1839 professor of chemistry and physiology in New York University, later president of the faculty of science. He was the first president, in 1876, of the American Chemical Society.⁶ He published many papers⁷ and some interesting books.⁸ He experimented on phosphorescence.⁹

¹ *Elements of Chemical Philosophy*, 1812, 210 f.

² *A Popular Treatise on the Art of Photography, including Daguerriotype and all the New Methods of producing Pictures by the Chemical Agency of Light*, Glasgow, 1841 (viii, 96 pp.), 92.

³ *J. Chem.*, 1808, vi, 633-719.

⁴ *Prolusiones ad Chemiam Saeculi Decima Noni*, Buda, 1800, 141; *Accessiones Novae ad Prolusiones Suam*, Buda, 1800, 375 f., 383; see Vol. III, p. 599.

⁵ Ostwald's *Klassiker*, clii, 137, 198.

⁶ B. Silliman, *Amer. J. Sci.*, 1882, xxiii, 163; *Nature*, 1882, xxv, 274; Poggendorff, (1), i, 601; ii, 377; D. Fleming, *John William Draper and the Religion of Science*, Univ. Pennsylvania Press, 1950.

⁷ Collected in Draper, *Scientific Memoirs: being Experimental Contributions to a Knowledge of Radiant Energy*, 1878 (portr.).

⁸ *History of the Intellectual Development of Europe*, 1862 and later eds.; *History of the Conflict between Science and Religion*, 1874, 1875.

⁹ *Phil. Mag.*, 1851, i, 81-100; *Memoirs*, 133, 159.

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Draper¹ attempted to demonstrate the law that 'the chemical action produced by the rays of light depends upon the *absorption* of those rays by sensitive bodies'. He found that light reflected from one Daguerreotype photographic plate did not affect a second one, but Ascherson² could not confirm this. Draper³ then showed that a solution of ferric citrate absorbs what he called 'tithonic rays' (see p. 720) or active light, and is chemically changed, and that the transmitted light produces no more decomposition (the effect depends on the thickness of the absorbing layer and the extinction coefficient). Schultz-Sellack⁴ later proved, with silver halides, that optical absorption accompanies chemical action, and H. W. Vogel⁵ showed that certain organic dyes can sensitise silver bromide dry plates in the region of their own absorption, and hence yellow and red light can be made to act on the silver salts. Draper⁶ stated that the 'tithonic rays' producing chemical action are those which are absorbed by the substance. He later⁷ mentioned the experiments of Grotthuss for 'the discovery of the law under which these decompositions of the colours of flowers take place'; also the long paper by Herschel⁸ showing that 'the rays which are effective in the destruction of any given vegetable colour are those which by their union produce a tint complementary to the colour destroyed'.

Carey Lea⁹ failed to find any sensitising action of dyes on ferric oxalate, potassium chromate, uranyl nitrate, etc. The research of J. M. Eder¹⁰ was fundamental in the study of sensitisation by dyestuffs. J. J. Acworth¹¹ found a rough correlation between the absorption maximum of a coloured silver bromide gelatin plate and the maximum of chemical activity in the region of the spectrum, although this was always displaced towards the violet. The development of this work into 'panchromatic plates' is well known.

Chemical Photometry

A chemical photometer was first proposed by H. Benedict de Saussure, who found in 1787 that the rate of evolution of oxygen from chlorine water is proportional to the intensity of the light.¹² This was also proposed by Brugnatelli.¹³ Döbereiner¹⁴ found that hypochlorite decomposes faster in light than in the dark. W. C. Wittwer (privatdocent in Munich) measured chemically the disappearance of chlorine from dilute chlorine water exposed to light.¹⁵ He

¹ *Phil. Mag.*, 1841, xix, 195-210; *Memoirs*, 230.

² *Phil. Mag.*, 1845, xxvi, 465-78 (470).

³ *Ib.*, 1874, cliii, 218.

⁴ *Ib.*, 1872, xlv, 422-43; *Memoirs*, 412.

⁵ *Phil. Trans.*, 1842, cxxxii, 181-214: On the Action of the Rays of the Solar Spectrum on Vegetable Colours and some new Photographic Processes. J. F. W. Herschel used the name 'photography' in *Phil. Trans.*, 1839; he discovered that silver chloride is easily dissolved by a solution of sodium thiosulphate ('hyposulphite'): *Edin. Phil. J.*, 1819, i, 8, 396 (26 f., 398 f.), and suggested its use in 'fixing' to Fox Talbot, who used it early in 1839: Fox Talbot, *Compt. Rend.*, 1839, viii, 341 (letter to Biot); Herschel, On the Chemical Action of the Rays of the Solar Spectrum on Preparations of Silver... and on some Photographic Processes: *Phil. Trans.*, 1840, cxxx, 1-59.

⁶ *Amer. J. Sci.*, 1874, vii, 200.

⁷ *Ann. Phys.*, 1891, xlii, 371.

⁸ *Ann. Phys.*, 1871, cxliii, 161.

⁹ *Phil. Mag.*, 1845, xxvi, 465 (470); 1851, i, 368.

¹⁰ *Wien Ber.*, 1885, xc, II, 1097 (incl. hist.).

¹¹ *Ann. Phys.*, 1855, xciv, 597-612.

¹² *Effets chimiques de la lumière: Mém. Acad. Turin*, 1788-9 (1790), ix, 441-53; *Crell's Ann.*, 1796, I, 356-66.

¹³ *Crell's Ann.*, 1796, I, 373.

¹⁴ *J. Chem.*, 1813, ix, 12 (18).

¹⁵ *J. Chem.*, 1813, ix, 12 (18).

confirmed the law that with constant light intensity I , the chemical action is proportional to the chlorine concentration, c ; $-dc/dt = kcI$, where $k = \text{const.}$ Hence $\ln(c_0/c) = kIt$. He showed that the ratio of the initial to the final concentration c_0/c is constant for a given intensity and time, and also calculated It for a given c , finding it to agree with the formula. He assumed that the hydrochloric acid formed ($2\text{Cl}_2 + 2\text{H}_2\text{O} = 4\text{HCl} + \text{O}_2$) has no influence with very dilute chlorine water (0.1–0.4 p.c. Cl_2), but found¹ that below 0.1 p.c. Cl_2 the decomposition is faster than the formula requires. He tried to take account of the influence of the finite thickness of the absorbing medium, when the absorption of light is incomplete, but his mathematical investigation did not give a satisfactory result, and he used empirical formulae. G. Lemoine² obtained approximate results by taking account of the thickness, without overcoming all the difficulties due to the change of absorption coefficient during the reaction.

Wittwer's research was very sharply criticised by Bunsen and Roscoe,³ but Wittwer replied.⁴ He repeated his experiments (in Liebig's garden in Munich)⁵ and confirmed his previous results, and Ostwald⁶ said that Bunsen and Roscoe's criticisms went too far and Wittwer deserves more credit than they gave him.

Draper⁷ used a solution of ferric oxalate containing some ferric chloride, which decomposes to give a yellow precipitate of ferrous oxalate and evolution of carbon dioxide.

Eder⁸ used the reduction of mercuric chloride and ammonium oxalate solution to mercurous chloride, which was filtered and weighed: $2\text{HgCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 = \text{Hg}_2\text{Cl}_2 + 2\text{NH}_4\text{Cl} + 2\text{CO}_2$. Later work showed that a trace of ferric salt (normally present in the reagents) is necessary.⁹ A. R. Leeds¹⁰ determined the iodine liberated from an acidified iodide solution, but this depends on the variable amount of dissolved oxygen.

The 'galvanic photometer' of A. E. Becquerel consisted of two pure silver plates coated with silver iodide (sometimes chloride or bromide) immersed in acidified water and connected with a sensitive galvanometer. When one plate was illuminated, a current passed.¹¹ F. Griveaux¹² found that the action ceases when iodine is dissolved in the liquid round the illuminated plate.

The Hydrogen-Chlorine Reaction

W. Cruickshank¹³ made a mixture of 2 vols. of moist chlorine (prepared by the action of hydrochloric acid on potassium chlorate) and 1 vol. of hydrogen in a bottle. There was no immediate action but after 24 hours the gases had

¹ *Ib.*, 1856, xcvii, 304–10.

² *Compt. Rend.*, 1883, xcvii, 1268–12; 1891, cxii, 936–9, 992–5.

³ *Ann. Phys.*, 1855, xcvi, 373–94.

⁴ *Ann.*, 1865, Suppl. iv, 63–79.

⁵ *Memoirs*, 265.

⁶ *Wien Ber.*, 1879, lxxx, II, 636–60.

⁷ *Phil. Mag.*, 1880, x, 89–97.

⁸ *Phil. Mag.*, 1880, x, 89–97.

⁹ *Compt. Rend.*, 1839, ix, 561–7; 1841, xiii, 198–200; *Ann. Chim.*, 1843, ix, 257–322; 1851, xxxii, 176–94; L. G. Gouy and H. Rigollot, *Compt. Rend.*, 1888, cvi, 1470–1; Rigollot, *Ann. Chim.*, 1891, xxii, 567–74; G. M. Minchin, *Phil. Mag.*, 1891, xxxi, 207–38.

¹⁰ *Compt. Rend.*, 1888, cvii, 837–9.

¹¹ *Nicholson's J.*, 1802, v, 202; September 1801.

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combined completely. He does not mention the effect of light, to which the mixture must have been exposed for part of the time. He found that on explosion by an electric spark 'three measures of hydrogenous gas requires three and a half of oxygenated muriatic acid gas to saturate them; the products being water and muriatic acid'. The explosion of a mixture of equal volumes of hydrogen and chlorine on exposure to sunlight was reported by Gay-Lussac and Thenard:¹ 'the jars were reduced to splinters and projected to a great distance.' The gases did not combine in 8 days in the dark but the colour of the chlorine disappeared in 15 mins. in ordinary daylight. They thus proved that the reaction depends on the light intensity. Explosion was also brought about by an electric spark or by iron heated to 150° (doubtful). The results were communicated by Berthollet to Gehlen.² Gay-Lussac and Thenard say: 'l'acide muriatique oxigéné, dissous dans l'eau, n'est décomposé par la lumière que parce qu'au moyen du fluide lumineux les molécules de cet acide se trouvent élevées à une haute température',³ but Davy⁴ opposed the idea that the chemical action of light is due to a heating effect. Berthollet⁵ had pointed out that the chemical effects of light and radiant heat are very different.

Thenard⁶ said the mixture of chlorine and hydrogen combined but did not explode in ordinary daylight because the light was absorbed only in the layer of gas in contact with the wall of the jar: 'c'est à dire, que tous les rayons capable de produire l'action chimique sont absorbés par cette couche.' Silliman⁷ prepared a sensitive mixture of hydrogen and chlorine which *exploded* in ordinary daylight, direct sunlight not being necessary, and Bunsen and Roscoe⁸ prepared pure mixtures free from oxygen which exploded in feeble daylight.

Thomson⁹ says Dalton had informed him by letter that he had discovered that the mixture exploded in sunlight before Gay-Lussac and Thenard's results were published, and Dalton¹⁰ says that in June 1809:

'I made the mixture in a narrow eudiometer, and left it to stand over water; in about three quarters of an hour the greater part of the mixture had disappeared. In the next experiment, the gases, after being put together, seemed to have no effect, when suddenly the mixture began to diminish with rapidity . . . till in two or three minutes nearly the whole had disappeared.'

Dalton thus discovered what Bunsen and Roscoe later (see p. 721) called the period of 'photochemical induction'. In July 1809, Dalton says, he discovered the explosive union in sunlight.¹¹

J. W. Draper was the first to apply the rate of combination of hydrogen and chlorine to measure the intensity of light, using an apparatus which he called a

¹ *Mém. Soc. Arcueil*, 1809, ii, 349 (27 February 1809); *Recherches Physico-Chimiques*, 1811, ii, 129, 189.

² *J. Chem.*, 1809, viii, 495: undated letter.

³ *Recherches*, ii, 146.

⁴ *Elements of Chemical Philosophy*, 1812, 210; *Works*, 1840, iv, 154.

⁵ *Statique Chimique*, 1803, i, 192 f.

⁶ *Traité de Chimie*, 1813, i, 567; 1834, i, 144.

⁷ *Amer. J. Sci.*, 1821, iii, 341.

⁸ *Ann. Phys.*, 1857, c, 43 (66).

⁹ (2), 1817, i, 225.

¹⁰ *New System of Chemical Philosophy*, 1810, I, ii, 300.

¹¹ Mellor, *J. Chem. Soc.*, 1901, lxxix, 216; Dixon, *J. Soc. Chem. Ind.*, 1906, xxv, 145.

tithonometer (Fig. 58).¹ It was a glass U-tube closed at the top on one side and fitted on the other side with a vertical tube to serve as a liquid gauge, and pro-



FIG. 58. DRAPER'S TITHONOMETER.

vided with sealed-in platinum wires so that mixed gas, or either chlorine or hydrogen separately, could be generated electrolytically from commercial hydrochloric acid saturated with chlorine, with which the apparatus was filled. The tube was painted black except the clear top, which could be covered with an opaque cap. Draper found that when a mixture of hydrogen and chlorine is exposed to the light from an electric spark there is a powerful effect, 'the movement taking place and ceasing in an instant.' Mellor² and P. V. Bevan³ showed that this 'Draper effect' is due to the heat of combination of the gases. On normal illumination, Draper found, the amount of combination is, in general, proportional to the time with constant illumination, and is proportional to the light intensity (*Draper's law*).

Draper found⁴ that if a glass tube containing chlorine over saturated common salt solution is exposed to sunlight for a few minutes, then an equal volume of hydrogen added and the mixture exposed to daylight, the gas at once begins to combine; but in a similar tube which had been kept in the dark, the 'chlorine shows no disposition to unite with its hydrogen, and the liquid in its tube remains motionless for a long time'. (This was the photochemical induction period.) The effect persisted for several hours. In the formation of 'modified chlorine', 'a definite amount of chemical rays must disappear', and light which had passed through an insensitive mixture failed to bring about combination of a sensitive mixture. Draper found that the indigo ray in the spectrum is absorbed, not the violet as Bérard⁵ had stated. Draper assumed⁶ that 'modified chlorine' is an allotropic form, $Cl\alpha$, ordinary chlorine being $Cl\beta$. He thought he had shown that it is also produced in chlorine water exposed to light, since this continues to evolve oxygen slowly in the dark. He found that 'a ray which had passed through a given thickness of a mixture of equal volumes of chlorine and hydrogen lost by absorption just half as much of its original intensity as when it passed through the same thickness of pure chlorine gas' (cf. Bunsen and Roscoe, p. 722). He used a new apparatus in which the two gases were dried and collected in dry tubes. The chlorine in one tube was exposed to sunlight for half an hour, that in a second tube was kept in the dark. The gases were then mixed by sliding a glass plate with holes, and the hydrogen tubes opened over water. "The chlorine which had been exposed

¹ *B.A. Rep.*, 1843, ii, 9; *Phil. Mag.*, 1843, xxiii, 401-15; *Memoirs*, 1878, 245 (where it is called a 'photometer'); *Phil. Mag.*, 1845, xxvi, 465-78 ('tithonic rays'); it is named after Tithonos in Greek mythology, who 'shrunk in old age'; Dixon, *J. Soc. Chem. Ind.*, 1906, xxv, 145.

² *J. Chem. Soc.*, 1902, lxxxii, 1291.

³ *Phil. Trans.*, 1903, cii, 71.

⁴ *B.A. Rep.*, 1843, ii, 9; *Phil. Mag.*, 1844, xxv, 1-10; *Memoirs*, 271-83.

⁵ *Mém. Soc. Arcueil*, 1817, iii, 5 (35).

⁶ *Phil. Mag.*, 1845, xxvii, 327-46; 1857, xiv, 321-3; *Memoirs*, 284, 312.

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¹ *Ann. Ph.*
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² *Ann. Ph.*

to the sun united at once with its hydrogen' on exposure to light, but the other, which had not been exposed, showed a period of induction.

'It appears, therefore, that chlorine by exposure to the sun contracts a tendency to unite with hydrogen which is not possessed by chlorine which has been kept in the dark. . . . I infer that chlorine is one of these allotropic bodies, having a double form of existence. . . . As commonly prepared, it is in its passive state; but on exposure to the indigo rays or other causes it changes and assumes an active form.'

BUNSEN AND ROSCOE

A classical photochemical research is that of Bunsen and H. E. Roscoe on the union of hydrogen and chlorine.¹ They say that in Draper's tithonometer the pressure varied during the experiment and hence, since the amount of chlorine dissolved by the liquid varied, the composition of the gas was not constant. They used an apparatus which they call an *actinometer* in which the pressure remained constant.² It consisted (Fig. 59) of a half-blackened flat

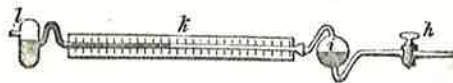


FIG. 59. BUNSEN AND ROSCOE'S ACTINOMETER.

glass bulb *i* (the *insolation vessel*), half-filled with chlorine water, which also partly filled a horizontal index tube *k*. A mixture of equal volumes of chlorine and hydrogen, obtained by the electrolysis of hydrochloric acid (sp. gr. 1.148, 30 per cent) with carbon electrodes, was passed through the apparatus for a long time. The bulb was then exposed to light from a coal-gas flame, passed through a tube of water; the hydrochloric acid formed dissolved in the chlorine water in the bulb and the liquid in the index-tube moved towards the bulb at a measured rate. Bunsen and Roscoe found the following results:

(1) At first there was no combination (a period of photochemical induction, varying with intensity of the light and the presence of impurities), then slow combination began, increasing to a constant rate which was proportional to the light intensity:

'The first action of light on electrolytic chlorine detonating gas is accompanied by a phenomenon of a highly peculiar kind, which we will discuss in more detail under the name of photochemical induction. The chemical action does not appear in its full strength at the moment of first illumination with completely constant illuminating power, but is first vanishingly, or nearly vanishingly, small, then increases gradually, reaching a maximum first after an appreciable time and then remains constant.'

Bunsen and Roscoe say that it had been believed that photochemical changes were not caused by light itself but by an agent different from light and

¹ *Ann. Phys.*, 1855, xcvi, 373-94 (criticism of Wittwer); 1857, c, 43-88, 481-516; 1857, ci, 235-63; 1859, cviii, 193-273; 1862, cxvii, 529; Bunsen, *Gesammelte Abhandlungen*, 1904, iii, 1-213; Ostwald's *Klassiker*, 1892, xxiv, xxxviii (does not include the last paper and an illustration is missing); *Phil. Trans.*, 1857, cxlvii, 355-80 (read 20 November 1856), 381-402, 601-20; 1859, cxlix, 879-926; 1863, clviii, 139-60; Roscoe, *Proc. Roy. Soc.*, 1862, xii, 648; *Phil. Trans.*, 1865, clv, 605-31; Roscoe and J. Baxendell, *Proc. Roy. Soc.*, 1867, xv, 20; Roscoe, in Watts, (1), 1873, iii, 678.

² *Ann. Phys.*, 1857, c, 43. The original apparatus is in the University of Manchester.

obeying different laws. They disproved this by showing that the effect followed the inverse-square law when the luminous flame was at different distances from the insolation vessel.

(2) The rates of combination were the same with the same light intensity if the apparatus was filled with fresh chlorine-hydrogen mixture, provided suitable precautions were used. Temperature within the range 18° to 26° had only a very small influence.

(3) When hydrogen and chlorine were prepared separately by the electrolysis of hydrochloric acid, and the chlorine either (a) sent in the dark to the insolation vessel, or (b) first passed through a 6 ft. glass tube exposed to bright sunlight, there was no change at all in the period of induction, whereas Draper had found that illuminated chlorine does not give rise to a period of induction. This result is described in their third paper,¹ which is completely concerned with photochemical induction. It mentions that Draper had found² that the activity of insolated chlorine lasts for weeks in the dark, whilst Bunsen and Roscoe found that it rapidly disappears. They say that affinity is an invariable force, but the particles of a body in following its action may experience a resistance, which is overcome by rise of temperature, or catalytic influence, or insolation (illumination): 'the act through which resistance to combination is decreased, and in consequence the state of more ready combination is brought about, we will call *chemical induction*, and designate it as photochemical, thermochemical, electrochemical, or idiochemical, according as light, heat, electricity, or chemical influences show themselves active in the removal of this resistance.' A similar classification was later proposed by Euler.³

Bunsen and Roscoe found that the 'induction maximum', when the rate of combination is proportional to the light intensity, is decreased to a small extent by adding hydrogen to the mixture, and to a marked degree by adding oxygen. They regarded the effect as catalytic. With $\frac{5}{1000}$ of oxygen the rate dropped from 53 to 5. Hydrogen chloride had no influence. This catalytic or contact action can be explained by the effect produced by a third particle *c* on the attraction of two particles *a* and *b* when it is brought within their sphere of influence, and the apparent difficulty that a very small amount of catalyst is active is also explained in detail.⁴ Bunsen and Roscoe⁵ found that the velocity curve for the action of bromine on a solution of tartaric acid has a point of inflexion, so that 'idiochemical induction' seems to be a result of 'the mode of action of the affinity force itself'.

Bunsen and Roscoe⁶ thought they had shown that more light is absorbed by a mixture of hydrogen and chlorine than by an equal quantity of chlorine alone (they showed that the absorption by hydrogen is negligible). They called this *photochemical extinction*.

Draper⁷ had previously found that the light absorbed is equal to that absorbed by the chlorine alone, and the non-existence of photochemical

¹ *Ann. Phys.*, 1857, c, 481-516.

² *Z. phys. Chem.*, 1901, xxxvi, 641.

³ *Ann. Phys.*, 1857, c, 481 (498).

⁴ *Ib.*, 510.

⁵ *Ib.*, 1857, ci, 235 (250).

⁶ *Phil. Mag.*, 1844, xxv, 1-10; *Memoirs*, 271.

⁷ *Phil. Mag.*, 1845, xxvii, 327; *Memoirs*, 296.

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⁸ *Abht.*

⁹ *Ib.*, 19

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¹⁰ *J. Chem.*

extinction was confirmed by careful measurements by C. H. Burgess and D. L. Chapman.¹

Lallement² exploded a $\text{Cl}_2 + \text{H}_2$ mixture by light from burning magnesium, and Hofmann³ by light from a burning mixture of nitric oxide and carbon disulphide vapour. Roscoe⁴ used thin glass bulbs filled with the gas mixture evolved from the electrolysis of fuming (30 per cent) hydrochloric acid.

Malaguti⁵ proposed a 'law of reciprocity' for photochemical changes, $It = \text{const.}$, where I = light intensity, t = time; i.e. a light of half the intensity acting for twice the time produces the same effect as light of given intensity acting for unit time. This was proved experimentally by Draper,⁶ who used an oil lamp with a constant flame and read the contractions of the tithonometer after 30, 60, 90 ... 210 secs. The movement for 30 secs. was constant in five different experiments. The light intensity was varied by screens used as sectors and the observed effects agreed closely with the calculated.

Bunsen and Roscoe⁷ confirmed the law by passing sunlight through a number of round holes of accurately measured diameter in a metal cap and receiving the images at such a distance that the visual angle of the openings was smaller than that of the sun. The photochemical effect was measured on sensitive silver chloride paper by a pendulum apparatus, and the photochemical effect within wide limits was proportional to the product of the intensity and the time of exposure. They prepared a 'normal' silver chloride paper for use in measurements of intensities. A comparison grey was prepared from zinc oxide, lampblack, and isinglass solution. The darkened paper was examined in sodium light. Roscoe⁸ and H. Vogel⁹ used standard silver chloride paper, exposed and fixed, as a comparison scale. This work, and Bunsen and Roscoe's¹⁰ on the chemical intensity of direct and diffused sunlight and light from the sky, was the basis of subsequent exposure tables. W. G. Hankel¹¹ used polarised light acting on sensitive paper, and by varying the intensity with a Nicol prism he found that the times required to produce equal changes of colour were inversely proportional to the intensities.

Draper's law (see p. 720), that the rate of combination of hydrogen and chlorine is proportional to the light intensity I , was accepted until E. C. C. Baly and Barker¹² found that the rate increased more rapidly than the light intensity. Mrs. Chapman¹³ found Draper's law nearly obeyed but the rate increased rather more slowly than the intensity. She used a smaller range of intensities than Baly and Barker. Allmand and Beesley,¹⁴ with light intensities varying from 1 to 440 and also polarised light, found the law obeyed, with

¹ *J. Chem. Soc.*, 1906, lxxxix, 1394 (1430).

² *Bull. Soc. Chim.*, 1865, iii, 178.

³ *Modern Chemistry*, 1865, 46.

⁴ *J. Chem. Soc.*, 1856, ix, 16; *Manchester Proc.*, 1865, iv, 101.

⁵ *Ann. Chim.*, 1839, lxxii, 5; *Ann. Phys.*, 1840, xlix, 567 (abstr.).

⁶ *Phil. Mag.*, 1843, xxiii, 401-15; *Memoirs*, 245, 264.

⁷ *Ann. Phys.*, 1862, cxvii, 529 (536).

⁸ *Ann. Phys.*, 1865, cxxiv, 353-90.

⁹ *Ib.*, 1868, cxxxiv, 146.

¹⁰ *Ib.*, 1859, cviii, 193-273.

¹¹ *Abhl. Sächs. Ges.*, 1864, ix, 53-90.

¹² *J. Chem. Soc.*, 1921, 653.

¹³ *Ib.*, 1924, 1521; G. Kornfeld and H. Müller, *Z. phys. Chem.*, 1925, cxvii, 242; 1925, cxviii, 476.

¹⁴ *J. Chem. Soc.*, 1930, 2693.

some tendency to Mrs. Chapman's finding at higher light intensities. D. L. Chapman¹ predicted that, with gases quite free from oxygen, the rate should be proportional to the square root of the light intensity ($I^{0.5}$), and Chapman and Gibbs² confirmed this by experiment. Norrish³ found practically the same result ($I^{0.6}$). The square-root law would follow if the primary process were a dissociation of the chlorine molecule into atoms at a rate proportional to the light intensity: $\text{Cl}_2 = 2\text{Cl}$, hence $[\text{Cl}]^2/[\text{Cl}_2] \propto I$. If the rate of reaction is proportional to the chlorine atom concentration, it would then be proportional to $I^{0.5}$. E. Budde⁴ observed that chlorine expands when exposed to sunlight, and he supposed that this was the result of a dissociation into atoms. He later⁵ showed that it is due to heating caused by absorption of light, but the phenomenon ('Budde effect') can be applied in an actinometer.⁶

Draper had found that inactive chlorine became active on exposure to light, whilst Bunsen and Roscoe found that exposure to light did not remove the period of induction produced when the treated chlorine was mixed with hydrogen. P. V. Bevan tried to explain the discrepancy.⁷ He concluded that something is formed in chlorine when exposed to light but this is washed out by bubbling through chlorine water, as in Bunsen and Roscoe's experiment, but not in Draper's. Strongly illuminated moist chlorine when suddenly expanded in the ratio 1:30 produced a fine rain of condensation nuclei, and a cloud when the ratio is 1:46. In the dark the cloud appeared only with the ratio 1:50. With the $\text{H}_2 + \text{Cl}_2$ mixture drops appeared with the expansion ratio 1:22 with illumination, but 1:42 in the dark. Bevan thought condensation nuclei of the type $\text{Cl}_2, \text{H}_2\text{O}$ are formed in illuminated chlorine, and hydrogen chloride is formed from a preliminary complex $\text{Cl}_2, \text{H}_2\text{O}, \text{H}_2$.

Van't Hoff⁸ suggested that an induction period is not peculiar to a reaction but is 'due to secondary actions' because 'some necessary precaution has been omitted'. C. H. Burgess and D. L. Chapman⁹ confirmed both Draper's and Bunsen and Roscoe's results with the types of apparatus used by the experimenters. They thought that in some glass vessels the induction period was shorter than in others, and that it was due to something dissolved from the glass. They then used a quartz bulb with a straight neck, containing calcium chloride solution, and filled it with $\text{H}_2 + \text{Cl}_2$ gas by heating to drive out some air, letting in gas, and repeating. With this apparatus no period of induction was found, which seemed to confirm their hypothesis. However, exactly the same result was found with a glass bulb. They finally traced the cause of the period of induction to organic nitrogenous impurities in the water ('albu-

¹ *Trans. Faraday Soc.*, 1926, xxi, 551.

² *Nature*, 1931, cxxvii, 854.

³ *Proc. Roy. Soc.*, 1933, cxl, 99, 713.

⁴ *Phil. Mag.*, 1871, xlii, 290; *Ann. Phys.*, 1872, cxliv, 213-19 (dated September 1876!).

⁵ *Ann. Phys.*, 1873, Ergzb. vi, 477-98.

⁶ A. Richardson, *Phil. Mag.*, 1891, xxii, 277-84.

⁷ *Phil. Trans.*, 1903, cii, 71.

⁸ *Études de Dynamique Chimique*, Amsterdam, 1884, 74, 82; *Studies in Chemical Dynamics*, 1896, 98; Mellor, *J. Chem. Soc.*, 1902, lxxxii, 1280 (bibl.).

⁹ *Proc. Chem. Soc.*, 1904, xx, 164; *J. Chem. Soc.*, 1906, lxxxix, 1399; Chapman, *Sci. Progr.*, 1912, vi, 657. David Leonard Chapman (Wells, Norfolk, 8 December 1869-Oxford, 17 January 1958), at first a schoolmaster, then assistant in Dixon's department in Manchester, became a fellow of Jesus College, Oxford (1907), where he equipped and directed the Sir Leoline Jenkins laboratories till his retirement. He proposed an important theory of the detonation wave (1899, see p. 632); Hamnick, *Proc. Chem. Soc.*, 1959, 101.

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¹ *Z. phys. Chem.*

² *Ib.*, 1909, xcvi,

³ *Proc. Roy. Soc.*

⁴ *Ann. Phys.*, 1872, Ergzb. vi, 477-98.

⁵ *Phil. Trans.*, 1903, cii, 71.

⁶ *Compt. Rend.*,

⁷ *J. Chem. Soc.*

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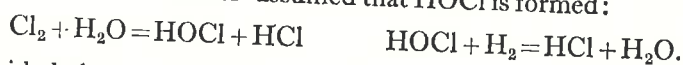
minoid ammonia') which was destroyed by prolonged reaction with chlorine. Ammonia and nitrogen trichloride were found to produce a period of induction. A hydrogen-chlorine mixture free from impurities reacted immediately on exposure to light, and the period of induction was a spurious effect, as van't Hoff had suggested.

Burgess and Chapman found that oxygen retarded the rate of combination but did not produce a period of induction. They thought the effect of ammonia or nitrogen chloride is probably purely physical; light puts the molecules, particularly chlorine, into a particular state of harmonic vibration and so renders them capable of combination. Impurities disturb this harmonic vibration; 1 molecule of NCl_3 in a million reduced the sensitiveness to $\frac{1}{100}$. Luther and Goldberg¹ and Chapman and P. S. MacMahon² confirmed that oxygen retards the photochemical union of hydrogen and chlorine. Chapman and MacMahon³ found that nitrous oxide and chlorine monoxide are inactive, nitric oxide, ozone, and chlorine dioxide inhibit the reaction. Norrish and Ritchie⁴ found that hydrogen chloride has a small inhibiting effect in mixtures free from oxygen, and hydrogen in mixtures containing some oxygen.

Much interest has been taken in the effect of moisture on the reaction. Ernst Pringsheim, Dr. phil. Berlin (1882), later professor of theoretical physics in Breslau, found⁵ that carefully dried gases do not explode on exposure to light but combination occurs completely. He assumed that water participates in the explosive reaction:



Veley⁶ and Gautier and Hélier⁷ assumed that HOCl is formed:



Veley divided the course of the reaction into four stages: commencement, inertness, reluctance followed by acceleration, constant velocity, and diminution of velocity.

Mellor⁸ found that addition of Cl_2O or HOCl did not produce any measurable effect, and Dixon and Harker⁹ found that once explosive reaction starts in the dry gas the detonation wave is faster (1795 m./sec.) than in the moist gas (1770 m./sec.).

¹ *Z. phys. Chem.*, 1905, lvi, 43.

² *J. Chem. Soc.*, 1909, xcv, 135, 952.

³ *Ib.*, 1909, xcv, 1717 (NO , N_2O); 1910, xcvii, 845 (O_3 , Cl_2O , ClO_2).

⁴ *Proc. Roy. Soc.*, 1933, cxl, 99, 112, 713.

⁵ *Ann. Phys.*, 1887, xxxii, 384; I have repeated the experiment successfully many times with gases dried by passing over phosphorus pentoxide.

⁶ The phases and conditions of chemical change: *Phil. Mag.*, 1894, xxxvii, 165-84.

⁷ *Compt. Rend.*, 1897, cxxiv, 1267.

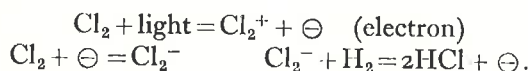
⁸ *J. Chem. Soc.*, 1902, lxxxii, 1291; Dixon, *J. Soc. Chem. Ind.*, 1906, xxv, 145. Joseph William Mellor (Huddersfield, 1869-Stoke on Trent, 24 May 1938), D.Sc. New Zealand, B.Sc. Manchester, pupil of Dixon, worked also on the effect of moisture on chemical change, etc. He became director of research in the Ceramic Institute, Stoke on Trent. His knowledge of chemical literature was unparalleled and his *Comprehensive Treatise on Inorganic and Physical Chemistry* in 16 vols. incorporates some of it: A. T. Green, *Nature*, 1938, cxlii, 281; *J. Chem. Soc.*, 1943, 341.

⁹ *Manchester Mem.*, 1891, iv, 3; Dixon, *Phil. Trans.*, 1893, clxxxiv, 97 (143). John Allen Harker (Alston, Cumberland, 23 January 1870-London, 10 October 1923), later in the National Physical Laboratory; Partington, *J. Chem. Soc.*, 1924, cxxv, 988; Poggendorff, (1), v, 499; vi, 1026.

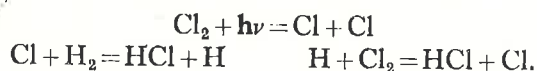
A new phase began with the work of M. Bodenstein and W. Dux,¹ who worked with a dry apparatus. They started with a mixture of hydrogen and chlorine and, after the reaction had proceeded some way, immersed the apparatus into liquid air, so freezing out remaining Cl₂ and the HCl formed, and measured the residual H₂ pressure. (Chapman thought that working with dry gases increased the danger of the effect of impurities.) Bodenstein and Dux found four main results; the velocity of reaction in presence of light is:

- (1) proportional to the square of the chlorine concentration but independent of the hydrogen concentration provided it is at least $\frac{1}{4}$ the Cl₂ concentration; with smaller amounts the velocity decreases slightly;
- (2) independent of the HCl concentration;
- (3) not influenced by water vapour within pressures of 0.004 to 2.3 mm.;
- (4) retarded by oxygen proportionally to its concentration. Hence $v = k \cdot [\text{Cl}_2]^2/[\text{O}_2]$.

To explain the discrepancy between (3) and previous work, Bodenstein and Dux assumed that when phosphorus pentoxide was used to dry the gas some oxygen was formed, which retarded the reaction. They supposed that chlorine is ionised by light:



But J. J. Thomson² had shown that chlorine, or its mixture with hydrogen, is not ionised by light, and the mixture when ionised does not react. Bodenstein and Dux³ then assumed that chlorine absorbs vibrational energy from light to form an active molecule, which reacts with H₂ to form active HCl molecules, which can give their energy to a Cl₂ molecule or to an O₂ molecule (which then keeps its energy). This theory of 'hot molecules' or an 'energy chain'⁴ seems very like Burgess and Chapman's theory. The modern 'atomic chain' theory was proposed by Nernst.⁵ A chlorine molecule absorbs a quantum of energy $h\nu$ from the light and dissociates into atoms. The following chain reaction is then set up, the chlorine atom being regenerated:



Only the first reaction is photochemical. The chains extend through the gas until they reach the walls of the vessel or an inactivating molecule such as O₂.

The fundamental law of modern photochemistry is the law of photochemical equivalence proposed by Einstein,⁶ according to which each molecule taking part in a photochemical reaction first absorbs one quantum of energy ($h\nu$) corresponding with the frequency (ν) of the radiation absorbed. (Some approach to this conception had been made by Stark in 1908.) This is the primary process in every photochemical reaction.

At least $3\frac{1}{3}$ million molecules of HCl are formed per quantum absorbed,⁷

¹ *Z. Elektrochem.*, 1913, xix, 836; *Z. phys. Chem.*, 1913, lxxxv, 297.

² *Proc. Camb. Phil. Soc.*, 1901, xi, 90.

³ *Z. Elektrochem.*, 1916, xxii, 53.

⁴ J. A. Christiansen and H. A. Kramers, *Z. phys. Chem.*, 1923, civ, 451.

⁵ *Z. Elektrochem.*, 1918, xxiv, 335.

⁶ *Ann. Phys.*, 1912, xxxvii, 832.

⁷ Bodenstein, *Z. Elektrochem.*, 1932, xxxviii, 911; Allmand, Craggs, and Squire, *J. Chem. Soc.*, 1937, 1869.

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whilst Einstein's law of photochemical equivalence requires one molecule decomposed per quantum ($\text{Cl}_2 + h\nu = 2\text{Cl}$, giving 2HCl). The higher yields are due to subsequent non-photochemical chain reactions. Weigert and Kellermann¹ illuminated the mixture with a spark lasting 10^{-6} sec., then examined with light not absorbed by chlorine. Nothing was seen at first, then convection streaks appeared, reaching a maximum after $\frac{1}{100}$ sec. (dark reaction) and disappearing after $\frac{1}{20}$ sec.; these were due to spreading of chains causing heat evolution.

Nernst's scheme does not include the marked effect of moisture discovered by Pringsheim (see p. 725). Dixon and Harker (see p. 725) found that the light intensity needed to explode an $\text{H}_2 + \text{Cl}_2$ mixture dried by P_2O_5 is much greater than for a moist mixture. H. B. Baker² showed that a very pure $\text{Cl}_2 + \text{H}_2$ mixture dried by redistilled pure P_2O_5 combined at a rate 'incomparably slower' than the moist gases under similar conditions. Bodenstein and Dux (see p. 726) found no effect on drying with concentrated sulphuric acid but Tramm found that the effect of drying is not appreciable until much drier gases than this are used.³ A very pure and dry mixture was unaffected by visible light. When the water vapour pressure was less than 10^{-7} mm. there was no reaction but with 10^{-5} mm. there was reaction.

Tramm cleaned the reaction vessels and dried them by *strong* heating under a high vacuum, which is necessary to remove moisture from the glass. Every precaution was taken to prevent oxygen and inhibitors entering the gases. The hydrogen was dried by keeping for a long time at liquid air temperature. The chlorine was first prepared by heating potassium dichromate and hydrochloric acid, but later⁴ by heating gold chloride, and was dried by distillation and fractionation at low temperature and pressure. F. Bernreuther and Bodenstein⁵ maintained, however, that water vapour is not necessary for the combination in visible and ultraviolet light and suggested that previous results were due to impurities, e.g. the presence of gold chloride in chlorine made by heating this, or silicon chloride formed by the action of chlorine on a silica vessel, and Coehn and May⁶ agreed with this improbable suggestion. The work of Allmand, Craggs, and Squire,⁷ who found that water vapour retards the reaction, was not carried out with sufficient attention to experimental details and requires confirmation.

Photosynthesis

An account has been given (see Vol. III, p. 277) of earlier work on photosynthesis. Some interesting experiments were made by Daubeny.⁸ By using

¹ *Z. Elektrochem.*, 1922, xxviii, 456; *Z. phys. Chem.*, 1923, cxvii, 1.

² *J. Chem. Soc.*, 1894, lxxv, 611; *Nature*, 1933, cxxxii, 27.

³ *Ber.*, 1923, lxxvi, 458; *Z. phys. Chem.*, 1923, cxv, 536.

⁴ Coehn and Jung, *Ber.*, 1923, lvi, 696; *Z. phys. Chem.*, 1924, cx, 705.

⁵ *Sitzb. Berlin Akad., Phys. Kl.*, 1933, vi, 333-55.

⁶ *Z. phys. Chem.*, 1934, xxviii, 126.

⁷ *J. Chem. Soc.*, 1937, 1869, 1878, 1889.

⁸ *Phil. Trans.*, 1836, cxxvi, 149-75 (read December 1835): On the Action of Light upon Plants, and of Plants upon the Atmosphere. Charles Giles Bridle Daubeny (Stratton, Glos., 11 February 1795-Oxford, 13 December 1867) succeeded Kidd as professor of chemistry in Oxford in 1822 and in 1834 also became professor of botany. He published *A Description of Active and Extinct Volcanos*, 1826; *An Introduction to the Atomic Theory*, Oxford, 1831; *Supplement*, 1840; 2 ed., 1850; *Essay on the Trees and Shrubs of the Ancients*, Oxford, 1865.

sunlight passed through various coloured media, and leaves in jars of water saturated with carbon dioxide, he showed that in the assimilation of carbon dioxide by plants yellow light is absorbed, whilst the blue 'chemical' rays have little action. This contradicted the earlier idea that the blue, violet, and ultraviolet rays alone gave rise to chemical action. J. W. Draper¹ confirmed Daubeny's results, using a spectrum and seven glass tubes containing a solution of carbon dioxide with a leaf of grass in each, and also coloured glasses. He later² gave a summary of work proving that 'every part of the spectrum, no matter what its refrangibility may be, can produce chemical changes, and therefore there is no special localization of force in any limited region'. The part absorbed is, of course, usually different in different reactions.

That the oxygen set free in photosynthesis comes from water was suggested by Berthollet:³ the oxygen is set free 'because light combines with the dephlogisticated air and imparts to it its gaseous form', and the hydrogen is formed 'par la décomposition de l'eau dont le gaz inflammable entre probablement dans la composition de leurs parties huileuse et résineuse'. This view was also held by H. E. Armstrong (see p. 801). The reaction is probably very complicated, but the nascent hydrogen also produced reduces carbon dioxide to substances from which carbohydrates $(\text{CH}_2\text{O})_n$ are ultimately produced:⁴



R. W. Gunther, *History of the Daubeny Laboratory, Magdalen College, Oxford. To which is appended a list of the Writings of Dr. Daubeny. With a preface by T. H. Warren* [President of Magdalen College], London, 1904; *id.*, *Early Science in Oxford*, Oxford, 1926, iii, 210 f.; J. R. Green, *A History of Botany in the United Kingdom*, 1914, 422; Bettany, DNB, 1888, xiv, 94; W. De la Rue, *J. Chem. Soc.*, 1868, xxi, pp. xviii-xxi.

¹ *Phil. Mag.*, 1843, xxiii, 161; 1844, xxv, 169; *Memoirs*, 1878, 167, 184.

² *Phil. Mag.*, 1872, xlv, 104, 422; *Memoirs*, 404: on the distribution of chemical force in the spectrum.

³ *Obs. Phys.*, 1785, xxvi, 321; AdS, 1785 (1788), m 276.

⁴ Ruben *et al.*, *J. Amer. Chem. Soc.*, 1941, lxiii, 877; Dole and Jenks, *Science*, 1944, c, 409; Calvin *et al.*, *ib.*, 1948, cvii, 476; 1949, cix, 140; *J. Chem. Soc.*, 1956, 1895.

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³ *Ann. Phys.*

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⁷ *J. Chem. Soc.*

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