the quantum yield: an historical perspective

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The 19th century, when Grotthuss still saw light as a line of elements of *Aether* with undetectable separation[1] and Draper[2] explained that photochemical reactions depended on compounds sensitive to incident radiation, came to a close with a paradigm shift.[3] This accompanied, or was driven, by the tremendous changes occurring throughout society at the turn of the 20th century. Even rural areas of America were being electrified and the light bulb was soon to replace the kerosene lantern in houses across the country. Telephones appeared, the auto arrived and little towns were made safer by community water supplies. The last years of the 19th century also saw enormous intellectual resources expended in German research institutes[4] that were funded collaboratively by industry and the government and directed to develop, among other things, new ways to produce electric lighting. The emission of light from heated so-called "black bodies" represented one possibility for converting electricity into light that was studied in detail by physicists and engineers at the PTR[5] in Berlin of which Werner von Siemens was a member of the board. The seamless connection between these institutes and industrial collaborators was elaborated by the Board of Directors. Wien's[6] equation, and experiments on emissions from black bodies by Pringsheim, Lummer and especially Rubens triggered Planck's law which appeared in December 1900.[7] Planck defined the natural constant h (h = 6.55 x 10^{-27} erg x sec) and used equation 1 to successfully model the recorded spectra of light emitted from black bodies. The energy E is composed of a specific number of finite, equal parts the number of which can be calculated by multiplying the frequency, ν, by the constant h which yields the energy element e (erg) of the oscillator. Planck termed these parts *quanta* (meaning "how much" in Latin).

$$E = \frac{8\pi h\nu^3/c^3}{e^{h\nu/kT} - 1} \qquad (1)$$

A little later Einstein, secluded in Bern, worked on physics in the evening following a day at the patent office. Perhaps beneficially he was not tied to any of the Berlin groups, and was, therefore, unaware of certain salient papers in the field. The first[8] of four papers in 1905 on the *photoelectric effect* was just one that established his legacy and the work for which he was awarded the Nobel Prize. Though Einstein did not use the word *photon* (that insight goes to Gilbert Newton Lewis),[9] he did postulate that light was discontinuous and suggested that light is comprised of indivisible moving energy quanta *that can only be absorbed or created in discrete units*. Einstein based this on several specific examples other than black body emissions such as the creation of cathode rays by UV light.[10] He argues that a view in which light was continuous had to be incorrect because it contradicts the observation of the photoelectric effect[11] and he goes on to theorize that the photoelectric effect is triggered by light quanta impinging on a material surface where the energy of said light quanta are at least partially transformed into electrons with a kinetic energy E_{kin} (equation 2). If the energy of each *quant* of incident radiation is independently transferred to an electron, then the velocity of the electrons emitted is independent of the intensity of the incident radiation. On the other hand, the number of ejected electrons *is* proportional to the intensity of the incident light.

$$E_{kin} = \frac{R}{N}\beta\nu - P \qquad (2)^{12}$$

By 1908 Johannes Stark, whose work was overlooked for a while, had reported the first application of the quantum hypothesis to photochemistry.[13] He defined that a direct photochemical reaction consists of first a chemical absorption (light-triggered ionization) reaction and second a light independent reaction. Stark proposed that the valence electrons of unsaturated and carbonyl groups in organic compounds are responsible for UV absorption. In his third law of photochemical reactions, Stark reports proportionality between the intensity of the effective light and the conversion of the photochemically transformed compound in a unit time—an obvious recognition of what became *quantum yield*.

Einstein legitimately surfaced in the cult that better enabled scientific communication of the day at the first Solvay Conference in 1911.[14] Walther Nernst had fueled Ernest Solvay's interest in the *light debate* and the latter, a Belgian industrialist whose process produced 90% of the world's supply of soda by then, paid the travel/subsistence/honoraria that brought 23 leading physicists to Brussels for a scientific conference concerned with "Radiation theory and the quanta".[15] This conference gave birth to the most important experiments on the nature of light and its interactions with matter that lasted over the next decade and eventually confirmed Einstein's postulates. The concept of the quantum yield developed as a result.

In a 1912 paper from the Karl-Ferdinand University in Prague that followed the October Solvay Conference, Einstein[16] clarified the equivalence law with the further assumptions that "the decomposition of a molecule occurs as if the other molecules were not present" and that the

probability that a molecule decomposes in an increment of time ("Zeitteilchen") is proportional to the monochromatic light density (ρ). This is the *law of photochemical equivalence*, and it states that a photochemical decomposition of a gram-equivalent weight requires the absorption of Nhν (N = number of molecules in a gram-mol) light energy. The law follows the prerequisite that the number of decomposed molecules per time-unit is proportional to the density of the acting radiation. Though strictly speaking, the law of photochemical equivalence predicted that only dissociation reactions could be expected to obey it, by the mid-1920s[17] the matter had become clarified.

Emil Warburg,[18] called by Clark,[19] "the father of photochemistry" *[sic]* was told by Einstein[20] that he (the latter) thought that the number of primary photochemical processes is equivalent to the number of wavelength-specific Planck's energy elements contained in the absorbed radiation. Using equations of the "Einsteinschen Satz" and the "Wien-Planckschen Strahlungsgesetz", Warburg thus calculated that the theoretical yield of the primary photochemical process of the ozonolysis of oxygen ($3\ O_2 \rightarrow 2\ O_3$) at 209 nm to be 50% and in later experiments measured a yield of 46% based on the number of "photons" absorbed. This was the first literature example in which the quantum hypothesis predicted an estimation of the upper yield of the primary photochemical process.

Warburg's observations on the photochemical formation of ozone lead to the question "is it the frequency of the incident radiation or the frequency of the absorbing molecule ('Eigenfrequenz') that is responsible for the amount of energy absorbed per molecule decomposed?". Einstein[21] had postulated that it is the frequency of the incident radiation and it is he who first explains this, in his answer to Warburg's questions. On the last page of his 1912 paper, he indicated, for the first time, that *the energy carried by each light quantum is* $e = h\nu$.[22] Specifically, he also deduced that the absorbed energy per molecular decomposition is only dependent on the frequency of incident radiation.[23]

The Bohr model of the atom (1913),[24] familiar to every high school student,[25] caused Einstein to deduce a rationalization for the energy changes resulting from the emission of an electron from an atom. This further clarified what he meant by a photochemical event and suggested a way to at least partially explain the resulting atomic spectra.[26]

An early theory of photochemical kinetics, that of Bodenstein,[27] viewed the absorption process as a photoelectric process in which the first step is the scission of the absorbing molecule into the "*positiven Rest*" and electrons. The immediate reactions of the "*positiven Rest*" were termed "primary light reactions", while the reactions of the *atom-like* electrons, which are dependent on other reagents and reaction conditions, were termed "light reactions" (equation 3).

$$R \xrightarrow{h\nu} R^+ + e^-$$

$$R^+ \longrightarrow \textit{primary photochemical reactions} \qquad (3)$$

$$e^- \longrightarrow \textit{light reactions}$$

Bodenstein calculated the energy (cal) of the absorbed radiation and the energy (cal) released from the decompositions of the photoproducts as two completely independent processes dismissing Warburg's attempt of 1912. *Post scriptum* Bodenstein admits to have missed the work of Lenard and Ramsauer, which contradicts the ionization event in chlorine and ozone, though he continued to insist on the integrity of his theory.

G. N. Lewis ("The Atom and The Molecule", 1916) elaborated on the classification of polar and non-polar compounds and on the valence bonding of compounds. In a separate paragraph on the color, Lewis describes that if a molecule is exposed to light of a frequency close to that of the molecule, the energy of the light is absorbed by setting the molecule in vibration. Compounds appear colorless if they do not absorb in the visible range and if their electrons are tightly bound. The more polar a compound, the more loosely held their electrons, the more shifted the absorption to the violet/blue and yellow appearance of the compound. If the absorption of the compounds is shifted to the visible range, then the compounds exhibit different colors, such as in the case of dyes. The extreme case is that of an alkali metal that is dissolved in liquid ammonia, which has a maximum absorption in the ultra-red and appears blue.[28]

Otto Stern was an Einstein assistant first in Prague and later in Zurich. In 1919 he and Volmer analyzed the lifetime of fluorescence of iodine vapors mixed with nitrogen and postulated that fluorescence results from the same molecular process as light emission after thermal and electrical excitation. They calculated the lifetime of iodine fluorescence to be ($\tau = 2 \times 10^{-8}$ s). Since Stokes' law applied, fluorescence was classified as a quantum effect. In a molecule capable of fluorescence, an electron is moving in a path of an enlarged radius compared to the ground state molecule. The quantum theory falls short on predicting the mean lifetime of excited species, therefore, Stern and Volmer turned back to classical theory to determine the lifetime of the molecules.

Warburg[29] was credited with defining an effective photochemical equivalent as the number of moles decomposed or converted by or through the absorption of 1 g-cal of

radiation, defining the unit φ as an experimental number that expresses a combination of all the primary and secondary processes leading to overall production of a product. P is the indicated photochemical equivalent as expressed in the number of excited molecules in moles per absorption of 1 g-cal. The qualitative ratio *(Güteverhältnis)* γ, is $\gamma = \varphi / p$. Warburg insists that the law of photochemical equivalence has limited validity, especially in cases where the excited molecules do not undergo photochemical reactions.

Stern and Volmer[30] analyzed the equivalent law using the Bohr-Einstein model of light absorption. Citing the work of Warburg, Nernst and Wolf, they rejected the hypothesis that the scission of the irradiated molecule is the primary photoreaction using iodine as an example. In fact, Bohr's proposal that the molecules undergo a change in the quantum state upon absorption of a *quant [sic]* with energy $h\nu$, is the primary photochemical process. The reactions of these primary photochemical products lead to the known products. Stern and Volmer verified that the published experimental results do not contradict Bohr's model.

By this time, Einstein's work on the nature of light had been sufficiently confirmed so that in 1921 he was awarded the Nobel prize in physics. His presentation of the Nobel lecture, however, was delayed until August 1922 because controversy remained about his theories. He was employed in a German research institute and the vestiges of World War I still hung heavily. However, the nature of light was now recognized,[31] and it was accepted sufficiently to have commanded the world's most important prize in physics.[32]

Winter[33] published a convenient method to determine absorption spectra of compounds in the UV region in 1923 while Bowen verified the equivalence law using solutions of chlorine oxides (ClO_2, Cl_2O) in carbon tetrachloride and discussed possible values of quantum yields.[34] In his second paper on photochemical decomposition of gaseous dichlorine monoxide, he reported a quantum yield of ≥ 2,[35] though the purity of these gaseous reactants tainted his results. Bodenstein and Kistiakowski,[36] who developed a method to purify chlorine monoxide, measured reaction kinetics as well as quantum yields for its decomposition in the gas phase. The quantum yield of chlorine monoxide decomposition was again measured as 2 and found independent of whether the reaction is stimulated through direct irradiation or sensitized with chlorine. These were nearly the first examples of which we are aware that overall chemical processes were included in the resulting quantum yields of product production.

Warburg exemplified and declared the quantum hypothesis a complete victory for the cases in which the equivalent law is applicable. If the quantum hypothesis is not applicable, the law delivers an upper limit for such reactions that is based on the primary photo processes. For those cases in which the quantum hypothesis is not applicable, Warburg closed by saying that the properties of "beanspruchten", that is, excited molecules under application of Bohr's model, such as lifetime, should be studied to find solutions.[37] Warburg suggested further investigation of the interaction of light with molecules, especially with respect to the *nature (in eine höhere Quantenbahn befördert) and lifetime (Verweilzeit) of the excited states.*

Gas phase experiments where manometry could be used to follow chemical change with molecules (compounds) of high energy content which might be thought to dissociate in a single step, were an early target of study. A significant advantage that developed as a result was that photochemical events were more easily controlled than runaway thermal reactions. Hydrazoic acid is, as most know, highly explosive. Arnold Beckman found no evidence that its photochemical reactivity generated an uncontrolled chain reaction even at pressures as high as 130 mm Hg and even though the irradiating wavelengths were in the deep UV.[38] There is no evidence that, if Beckman knew the word photon, he used it regularly because it does not appear in his Ph.D. thesis.[39]

Ramsperger[40] investigated the photochemical decomposition of azomethane using the mercury lines at 366 nm. Independent on temperature and pressure, he also observed a quantum yield of 2 for all the reactions. He postulated that "the energy transfer of the product (high in energy) of the first decomposition to a second molecule of azomethane causes the decomposition of the second molecule".

In a succinct paper in 1929, Bodenstein and Wagner[41] attempted to simplify the kinetic equations of photochemical reactions by defining 6.06×10^{23} quanta as one light equivalent. This is the first appearance of the term *Einstein* as the defined unit of a mole of photons.

The measurement of quantum yields for photochemical reactions of various kinds was an extraordinarily arduous process. In the first place there were no UV spectrometers, so spectra, had to be measured point by point. Secondly, there were no commercial light sources. Xenon bulbs and mercury resonance lamps were still experimental. The commercial photomultiplier tube also had not appeared. In the third place, there were few ways to follow quantitatively chemical processes. One of the best ways was to follow pressure change, so many of the early measurements were made in the gas phase using manometry. Beckman, working as a Ph.D. student with Roscoe Dickenson at Caltech,[39] studied the photochemical decomposition of hydrogen azide

(hydrazoic acid) to hydrazine[42] and ammonia.[43] Two other products were nitrogen and hydrogen. He followed total pressure and certain products individually only with gas phase techniques.

Beckman must have been an extraordinary experimentalist.[44] Some of the lengths to which he went to make the measurements are indicated below. His first vacuum line (Figure 1) included a quartz fiber manometer, H, he had modified himself in order to measure the absolute concentrations of hydrogen and nitrogen. Hydrazoic acid[45] was introduced from A and purified by freezing it out with liquid air at P. Once non-condensed contaminants (hydrogen and nitrogen) had been pumped off, it was admitted to the quartz cylinder marked N, 2.5 cm in diameter and 4.8 cm long that had flat windows on each end. The pressure of HN_3 in N was measured by a gauge, M. Following irradiation, liquid air was again applied at P and the pressure of the non-condensed gases measured with the McLeod gauge. The mole fraction of hydrogen in these gases was measured with the quartz fiber gauge H.[32]

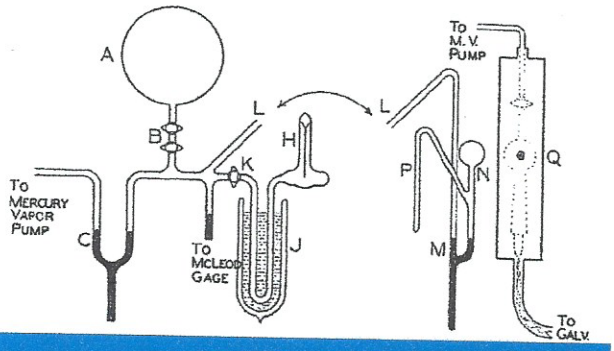


Figure 1. Schematic diagram of vacuum system.

Courtesy of ACS

Beckman used an aluminum electrode light source because its emissions could be controlled by passing the light through a monochromator, and the lines were approximately where hydrazoic acid absorbed. The light source was a spark produced between aluminum electrodes placed close to a monochromator. The flux of radiation was measured by vacuum thermocouple, Q, also constructed by the experimenter and described in detail in the paper.

Hydrazoic acid is transparent until about 220 nm and then shows strong lines at 199, 194, 186 and 185 nms. The absorption spectrum of HN_3 was measured by hand. This consisted of photographing a series of exposures of the radiation from the aluminum spark on the same photographic plate. A second photographic plate was imaged as a standard. In one-half of the cases the radiation was passed through the reaction cell empty. In the remaining cases the emission from the spark was passed through the cell with varying and increasing measured pressures of HN_3. The plates were calibrated for response with wire screens, and then the experimental plate photometered using the microphotometer of the Mount Wilson Observatory. The spark emission at 199 nm was isolated and used for the irradiation experiments, so the equivalent of the molar extinction coefficient at that wavelength was measured in a number of successive experiments. To measure the absorption coefficients at other wavelengths, an absorption at that wavelength was measured and this was bracketed by the absorptions of two of the wire screens. From the known absorption values of the screens, and known concentrations, the molar extinction coefficient could be calculated. The spectrum of hydrazoic acid measured this way is shown in Figure 2.

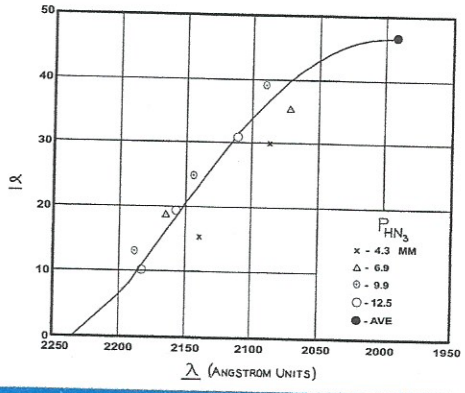


Figure 2. Light Absorption Coefficients, α of HN_3 as a function of wavelength.

Courtesy of ACS

Is it any wonder that in 1940 Beckman invented an absorption spectrometer and made particularly sure that it was useful in the UV?[46]

Quantum yields of HN_3 disappearance measured this way averaged about 3.0 with approximately 10% of the non-condensable product being hydrogen and the remainder being nitrogen. Yields were constant up to about 50 mm at which point they began to increase significantly presumably because hydrazoic acid decomposition began to follow chain reaction kinetics.

Beckman wrote a possible mechanism for the initial decomposition in which the primary step is conversion to HN and molecular nitrogen. He pointed out that even at 1950 Å the energy of the light absorbed is insufficient to produce individual atoms of N and H.

$$HN_3 - h\upsilon \rightarrow HN + N_2$$
$$HN + HN_3 \rightarrow NH_2NH_2 + N_2$$
$$HN + HN_3 \rightarrow H_2 + 2\,N_2$$
$$NH_2NH_2 + HN_3 \rightarrow NH_3 + N_2$$

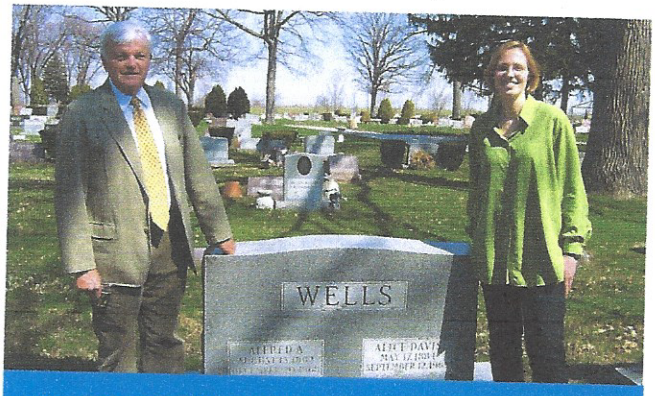
Beckman and Dickenson stated, "we regard the *ad hoc* invention of intermediate compounds as a pastime usually indulged in more for entertainment than for profit." So much for a lot of the work that has occupied Beckman spectrometers over the last 70+ years!

The first chemical actinometers of consequence were those using uranyl oxalate and developed practically and theoretically by Leighton and Forbes.[47] In the experiment, a 0.01 M solution of uranyl sulfate in 0.05 M oxalic acid was used as the standard. The quantum yield of the reduction of UO_2^{2-} to UO_2^{-} (or $HC_2O_4^{-}$) varies from 0.6 at 254 nm to 0.58 at 435 nm dipping to a minimum of 0.49 at 366 nm. Because of this variation it was later deemed inconvenient to use and eventually completely replaced by actinometers that used potassium ferrioxalate.[48] The latter was more versatile over a wide range of wavelengths, easy to use and both sensitive and precise. IUPAC published a report on the various methods of chemical actinometry quite recently.[49]

By 1938, Farrington Daniels was able to assemble a vast table of experimental data on quantum yields and explained that the deactivation of excited states by competing processes lead to a decrease in quantum yield below unity, while continuing reactions can result in a quantum yield of higher than unity.[50] "In the early development of quantitative photochemistry, it was believed by some that the Einstein relation would apply in many cases not only to the primary process of photoexcitation but also to the overall reaction as well. Quantum yields were summarized with the purpose of testing this hypothesis. Any hope of simplicity in chemical kinetics disappeared long ago."

The consequence of Beckman's work, and the work of many others that led to Farrington Daniels' extensive review in 1938 and the extraordinary compendium in English written in 1941, which Francis Heyroth said to be a second edition of "The Chemistry of Ultraviolet Rays",[51] essentially brought the boom initial period of photochemistry to a leveling off point that lasted until new experimental methods like spectrometers and chromatographs became commercial in the mid-1950s. By that time Beckman was well on his way to building the fortune that became his legacy, and the world of photoscience was able to use the fruits of his student labors in creative activity around the world.

Suffice it to say, chemical and physical measurements of quantum yields developed from these simple beginnings. It is appropriate, in this the 100th year anniversary of Einstein's publication on the photoelectric effect, to look at the history and reflect on it. Careful measurements over many, many years have brought quantitative photoscience to the stage it is today. And in spite of Beckman's exhortation that mechanism studies are more for entertainment than for anything else, have kept quite a few chemists and physicists occupied for many years. We propose they continue to do so well into the 21st century.



D. C. Neckers and Brigitte Wex at the grave of Alfred A. Wells, coauthor of the first American photochemistry book, *The Chemical Action of Ultraviolet Rays* (1925). The Center for Photochemical Sciences is located beside the cemetery which is in the middle of the Bowling Green State University campus.

Courtesy of BGSU

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11. Nobel Prize in 1921+.
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15. Dardo, M. In *Nobel Laureates and Twentieth-Century Physics*. Cambridge University Press: Cambridge, 2004; pp 83-84 and references therein. Einstein, whose first professorial position was in Prague, only completed negations to return to Zürich to take up the position in theoretical physics at the university in August 1912.
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17. For a review, see Allmand, A. J. *Trans. Faraday Soc.* **1925,** *21*, 438.
18. Warburg, E. *Sitzungsber. K. Preuss. Akad. Wiss.* **1912,** 216.
19. There are many biographies of Einstein and in this year many more can be expected. Occasionally, we have used Clark, R. W. *Einstein, The Life and Times*. World Publishing: New York, 1971.
20. Warburg says on p 224 footnote 1[18]: "Diesen Satz teilte mir Hr. Einstein auf dem Bruesseler Kongress 1911 mit, ..."
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31. Even Planck remained skeptical until experiments completed around 1915 convinced him.
32. The story is that Einstein's first wife, Mileva, requested Einstein's Nobel winnings as part of their divorce settlement. That was part of the settlement when the divorce became official in February 1919.
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