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PHOTONS IN CHEMISTRY AND BIOLOGY[1]

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I APPRECIATE the honor of being invited here and the privilege of living in beautiful Ithaca this semester. Wisconsin and Cornell Universities have always been close to each other. From the time of Babcock on, Cornell has sent many young men west to carry the inspiration of research to Wisconsin. Each university has vigorously directed the genius and energy of her students into useful paths.

My subject to-night is "Photons in Chemistry and Biology." The unit of light is the photon, the unit of chemistry is the molecule, and the unit of biology is the living cell. I propose to describe their general properties and their mutual interactions.

What do we know about light? We know that light affects the eye and makes vision possible. We know that light travels with an enormously rapid velocity—180,000 miles per second. We know that white light is made up of various kinds of light having different wave-lengths and that it is absorbed to a different extent by various objects through which it passes. When an object appears red we know that the blue and the yellow and the green and the other wave-lengths have been absorbed, leaving only the red to reach the eye.

When we ask the fundamental question as to what light is, we find ourselves in difficulties. The optical properties of light are very nicely represented by the hypothesis of a wave motion in a hypothetical ether. But this hypothesis is of little help in chemistry or atomic physics. In these fields we prefer to imagine a beam of light as a shower of photons—little bundles of radiant energy distributed in a random fashion in a beam, like bullets from a machine-gun.

On the other hand, this concept is of little use in

[1] A public address delivered at Ithaca, New York, on February 21, 1935.

describing the phenomenon of refraction and interference. So we have one and the same beam of light explained by two entirely different models. Obviously there is something incomplete about our pictures, and this incompleteness is always characteristic when we try to penetrate to fundamentals.

What do we know about chemical action? We know that all matter is made up of molecules which are characteristic of the particular substance involved, that all these molecules are composed of less than a hundred different atomic species, that only a score of these elements are at all common and that a dozen of these are necessary for life processes.

Our pictures of atoms and molecules change in style quite rapidly—from valence hooks, to electron pairs and cubes in 1916, to a maze of electrons rotating in elliptical orbits in 1923, and finally to the mathematical equations of wave mechanics of the present models. It is always a difficult problem to decide between complete accuracy and practical simplicity in the choice of hypotheses. In this case the wave equations are rarely used by chemists and the simple idea of valence is sufficient for elementary work, but the electron pair is useful for advanced work.

The phenomenon of chemical reaction can be interpreted in terms of energy better than in terms of mechanical models. We know that when chemical action takes place, atoms are transferred from one molecule to another. In order to make these transfers possible, it is necessary to introduce energy or, in other words, to activate the molecule.

This activation seems to be a necessary precursor to most chemical reactions, and the needed energy may be introduced in a variety of ways—by bombarding molecules with photons of light or with rapidly moving particles which have an electrical charge or by transferring the energy from a previously excited molecule. But in most ordinary reactions the activation is produced by collisions between molecules. There is satisfactory evidence that in any material above absolute zero the molecules are in a state of rapid, random motion, the velocity depending on the temperature. The probability-distribution of these moving molecules has been worked out with mathematical precision and checked by experiment.

Now the total number of collisions at room temperature increases only about 3 per cent. for a rise of 10° C., but most chemical reactions increase in velocity by 200 or 300 per cent. over this temperature range. It might appear, then, that there is no connection between molecular collision and chemical reaction, but it is only the few, very rapidly moving molecules which can supply energy sufficient to produce chemical activation, and their number is increased enormously by increasing the temperature.

What do we know about biochemical reactions? We know that living organisms exchange matter and energy with their environments and that they have the ability to reproduce themselves. The cells are composed of molecules, and the life processes are largely interpretable as chemical reactions and physical processes. I remember commenting to a biologist that biochemical reactions are very complex. Quick as a flash he retorted, "Yes, but so is any reaction in a test tube." I have had the truth of this statement vividly impressed on me during a fifteen-year study of chemical kinetics. We do not know what life is, but we do not even know what an atom is, or a photon.

We have surveyed briefly what is known in general terms of the fundamental units of light, chemistry and biology. We next turn our attention to mutual interactions between these different units and discuss the ways in which photons and molecules influence each other.

When a beam of white light is refracted by a prism it is spread out into its different wave-lengths—in other words, the various photons are placed in different places depending on the energy which they contain. The photons of greatest energy are displaced farthest from the direction of the original beam. Only the photons of intermediate energy are able to affect the human eye and give the sensation of light. Of these, the photons which give the sensation blue contain more energy than those which give the sensation red. Beyond the red lies the region called infra red, well known as heat radiations, and beyond these the long electromagnetic waves, familiar to any one who turns a radio dial. These photons have comparatively little energy. Radiation of wave-lengths shorter than the visible is termed ultra-violet. It contains photons of greater energy and it is refracted more. At still shorter wave-lengths and greater energy lie the x-rays, and beyond them the cosmic rays. The fundamental nature of radiation is the same throughout this whole range, but the chemical and biological effects are very different.

When radiation is passed through matter, some of the photons in the beam are stopped by molecules. A photon can be stopped by a molecule only when the molecule can rearrange its structure to take up just the amount of energy contained in the photon. Under these conditions radiation is converted into chemical energy or into heat. Even if the molecule is capable of this rearrangement it will not absorb the photon unless there is also an intimate collision between the photon and the molecule. Accordingly, the percentage of photons stopped depends on the ratio of molecules to photons, a fact which finds expression in Lambert's law regarding the thickness of the absorbing medium, and in Beer's law regarding the concentration of the absorbing solution.

Considerable progress has been made in visualizing the method by which molecules absorb the energy of the different photons. Heat radiations in the far infra red cause a molecule to rotate, while the photons in the near infra red cause the atoms in the molecule to stretch apart and vibrate. Photons in the visible region of the spectrum are able to make more violent changes. They can displace the electrons which hold the atoms together in the molecule. In the ultra-violet the mechanism is the same except that the energies involved are greater and the electronic displacements are greater. X-ray photons are more powerful still. They can be stopped only by doing a more drastic thing—namely, displacing an electron deep down within an atom near its nucleus.

It has been found that most chemical reactions which proceed with measurable velocity at and above room temperature require for activation roughly from 20,000 to 60,000 calories per gram molecule. This much energy is available in the photons of visible light. More than enough energy is available in ultra-violet and x-ray photons, but infra-red and radio waves are not able to bring the molecules to a sufficient state of activation to effect chemical reaction.

Our guiding principle in the understanding of radiation is the quantum theory. The most important expression of this theory for chemists is the Einstein law of photochemistry, according to which one molecule is activated for each photon absorbed. It must be remembered that after a molecule becomes activated a great many things may happen to it, and only rarely does each activated molecule produce one molecule of a new chemical product. The phenomena are so complex that actual experimental proof of this law is very meager, but it is generally accepted and useful.

The photo-chemist is not concerned with the amount of light that *passes through* the reacting system; he wants to know how many photons are *absorbed* by the reacting system. He then measures the number of molecules reacting, and this ratio of molecules to absorbed photons gives him valuable information regarding the mechanism of the process. If the ratio is unity, the reaction is probably a primary reaction to which Einstein's law applies. If it requires many photons to make one molecule react, there are complications, and either some of the activated molecules are dissipating their energy as heat, or a second reaction is taking place in such a way that it is not noticed, or thirdly, a reverse reaction is offsetting the photochemical reaction.

On the other hand, if the ratio of molecules to photons is greater than unity a chain reaction is involved. One molecule becomes excited and the product of the reaction is able to activate another molecule, and many molecules simply follow blindly after the leader, like a series of ten pins. Carried to extremes the chain reaction may become an explosion. The investigations of photochemistry offer excellent opportunities for studying chain reactions, and it is becoming increasingly apparent that they are very common in both chemistry and biology.

We have been discussing the chemical action of photons on molecules. Let us look for a minute at the reverse process in which chemical reactions emit photons—the phenomenon of chemiluminescence. You are familiar with phosphorescent substances, such as decaying wood, or phosphorus glowing in the dark, or bacteria in sea water being oxidized as a boat plows through the water. Perhaps the most striking illustration of all is the ordinary firefly. In all these phenomena a chemical reaction gives rise to the displacement of an electron (or atom) in a molecule, and when the electron falls back into its normal position of lower energy, a photon of radiation is emitted. At first sight one wonders why the phenomenon of chemiluminescence is not more common than it is. Apparently rather special conditions must exist. The absorption must be slight in order that the photons emitted in the interior of the reacting medium can escape and be detected. Again, unless this particular photon happens to fall in the energy region corresponding to visible light, the chemiluminescence will not be detected by the eye. It is quite likely that intensive searches for chemiluminescence in the infra-red region of the spectrum may show that chemiluminescence is a fairly common phenomenon.

Turning next to photo-biology, I want to emphasize that this field is but a special application of photochemistry. The effects produced in living matter by photons are due merely to ordinary photochemical reactions in which the photons displace electrons within the molecule, and the molecule then rearranges or combines with other molecules. I shall confine my remarks to a few specific cases of photo-biology.

I have always wondered that more attention has not been paid to the fundamental process of photo-synthesis by chlorophyll in green plants. Millions of dollars have been spent in agricultural experiment stations on applied problems, but only a few laboratories have ever been concerned with a study of the primary process which lies back of all plant growth. It is a process of extraordinary importance, since it supplies the material which provides the energy of animals and man and the energy of engines. Chlorophyll is a complex organic substance which absorbs photons in the visible region of the spectrum, and in the plant causes carbon dioxide and water to combine, giving various carbohydrates and a number of more complex organic substances.

The mechanism by which carbon dioxide and water unite in the presence of chlorophyll and photons is by no means understood. It is clear that over 100,000 calories of energy are required for the production of a gram molecule of material and that the photons of visible light do not contain as much energy as this. Only in the very short ultra-violet would one expect the photons to be sufficiently powerful to cause the direct union of carbon dioxide and water. However, the living cell *does* use visible light, and the manner in which it is able to combine several of these photons of lesser energy in such a way as to bring about this important reaction is a matter of great interest. It is unique in photochemistry.

Passing next to mitogenetic rays it must be emphasized that this subject is still controversial. About ten years ago a Russian investigator, Gurwitsch, reported that rapidly growing cells, such as the tip of the onion root, emit radiation of short wave-lengths and are able to accelerate growth in neighboring cells. This mysterious radiation was able to penetrate quartz, but unable to penetrate glass. Several hundred papers have followed in this field, but the results are in no way conclusive. Some investigators find mitogenetic rays emitted by a variety of living tissues, and increased growth has been reported in yeast cells, in young bacteria and in certain plants. Obviously a more reliable check of these mitogenetic rays would lie in detection by physical means, such as photographic plates and ionization chambers. Unfortunately, the photographic plate is far too insensitive to be considered. Very sensitive Geiger chambers have been used, in which a photoelectric effect is combined with an amplified ionization current so as to register electrical currents when a few individual photons enter the chamber. Some investigators have reported positive effects with Geiger chambers, but others have failed. There is no fundamental reason why some chemical reactions occurring in life processes should not emit photons. We have discussed this matter already under chemiluminescence. But whether or not such radiations, if they exist, have any biological significance is a matter for the future to decide.

You are familiar with the use of infra-red lamps for physical therapy. These photons in the infra-red are able to penetrate animal tissue beyond the surface layer. The energy which they contain is not enough to bring about chemical reaction, but they penetrate deeply and dissipate their energy as heat. In other words, infra-red radiation offers a convenient means for heating tissue considerably below the surface, and in this way it is possible to increase circulation of blood or bring about improvement in stiff joints and in certain diseases. The photons in visible and in ultra-violet light are stopped at the surface, but at still shorter wave-lengths we get the deeply penetrating x-rays. Since the photons of x-rays contain large amounts of energy they can bring about violent reactions and destroy tissue either at the surface or deep in the body. Gamma rays from radium are similar in character to the x-rays, and both of these agents are useful in the destruction of rapidly multiplying cells such as are found in cancer.

One of the most intriguing applications of photochemistry to biology is that of the mutations produced by x-rays, as discovered by Muller in his study of fruit-flies. Fruit-flies have been studied from a genetic standpoint for a long time, and experts are able to predict with considerable certainty the number of new variations which may be expected in a pedigreed colony. These variations include color of eyes and various biological characteristics which might not be evident to an inexperienced observer. When these fruit-flies are exposed to x-rays before breeding, the number of variations in offspring is greatly increased. This same phenomenon has been found in various other organisms—in the much-studied and pedigreed tobacco plant, for example. Through remarkable advances in microscopic technique it has been found that this x-ray treatment actually dislocates certain cells in the chromosomes which control the hereditary features. These dislocations of the chromosomes give a mechanical picture which agrees perfectly with the hereditary features as catalogued by the geneticist. The photochemist can claim this as one of his reactions. A photon hitting a vital spot in the cells of a chromosome is able to start a chemical reaction which on multiplication gives this mechanical distortion which in turn leads to the variations in the species. The penetrating photons of x-rays are thus uniquely favorable for bringing about changes inside the cell, and any mechanical stimulus designed to produce the same effect would be impossible because of the attendant destruction of the cell. The question arose as to whether all naturally occurring mutations may not be caused by photons coming from the deeply penetrating but rather infrequent cosmic rays or from gamma rays in traces of radio-active material. Certainly the naturally occurring mutations, which make possible biological evolution, can be explained in part as photochemical reactions, but the number of mutations appears to be considerably greater than can be completely accounted for by this mechanism.

The cure of rickets by ultra-violet light constitutes one of the most interesting chapters in photo-biology, and because of the intensive work which has been done in this field we are able to draw rather definite conclusions. Ten years ago it was thought that the radiation produced some mysterious effect in an animal in such a way that calcium was deposited in a normal manner in the bones. Some thought that the photons themselves were the primary cause of the calcium deposition. When Steenbock found that the radiation of food was just as effective as the radiation of the patient, the problem obviously became one of simple photochemistry. Separating the various parts of the food it was soon found that the cholesterol, later ergosterol, was the material which, when acted upon by light, brought about the normal deposition of calcium. Little was known about the actual vitamin D or the mechanism involved. In a cooperative research with Professor Steenbock, starting in 1927, we determined the minimum amount of energy of ultra-violet radiation necessary to prevent rickets in a rat. From this value we calculated the number of photons and the number of molecules, on the assumption that the Einstein law applied. Assuming further that the molecular weight of vitamin D is practically the same as that of its precursor, ergosterol, we calculated that 60 billionths of a gram should be a sufficient dosage to prevent rickets in a rat. Two years later, Bourdillon and Webster produced the practically pure vitamin D and found that 50 billionths of a gram was necessary, a quantity which was practically identical with the prediction based on photochemistry.

When Steenbock discovered the effect of irradiating food with ultra-violet light, he saw the social implications of his discovery. He saw a gullible public swayed by the word "vitamin" and the word "radiation"; he saw an American dairy industry competing strenuously with butter substitutes, and a Norwegian fishing industry largely dependent on the production of vitamins. He realized that every corner drug store could radiate its own vitamin D and that it would be years before the government could get things standardized. People would buy material that was dangerously over-irradiated and worthless material that was under-radiated. Here was a "baby on the doorstep," and something had to be done. He took his discovery to the university, but the university was not equipped to handle it. He was offered a large sum for the discovery, but he did not want it. He pioneered along new lines, and the Wisconsin Alumni Research Foundation was organized. Alumni of the university, busy business men, serving without pay, control the policies and give the profits to the university to support further research. Neither the university nor any of its faculty has anything to do with the foundation's business or policy. The university simply accepts without any strings the moneys which the foundation gives it, and a faculty committee allocates it where it will do the most good in furthering the research program of the university.

The social implications of research are enormous. The scientist can no longer toss his bombs of discovery promiscuously on a helpless humanity without warning. He must cooperate with the social scientist and the statesman. The problem of obsolescence must be faced.

Take a specific case, hypothetical, but not beyond the realm of possibility a few decades hence. Suppose that botanists, photochemists, organic chemists and engineers, working together, are able to synthesize food material on a commercial scale from carbon dioxide and water, using sunlight and some kind of an artificial chlorophyll in which the living plant and the soil are not necessary. What should be done with such a discovery? It would be hailed as a remarkable achievement and an insurance against world starvation in case of enormous over-population, an unprecedented period of drought or the advent of another ice age. The tropical and arid regions with sunshine, but little soil, could produce the necessary food in troughs instead of in plowed fields. But what about the effect on the chief industry of the world—agriculture; and all the human and economic factors which are interwoven with it? There are enough difficulties in this field already without bringing in new competition. Research along these lines and all others must be given every encouragement because no one knows what is ahead, and a reserve stock of scientific knowledge is the best equipment for emergencies and for new improvements. In the *application* of scientific discoveries to human affairs, however, the most unselfish and far-visioned statesmanship is necessary. Advance warning and cooperation by scientists and slow development through a transition period to allow economic readjustment are necessary. The principle that those who profit by a new application must help those who lose by it should become well recognized.

Nothing which I have said must be taken to imply any regimentation in or dictatorship of scientific research itself. Scientific research is spontaneous and must not be spoiled by interference. Cooperation between scientists is absolutely essential—but it already exists. It is thrilling to see how scientific advances come about through the unconnected and independent efforts of different men publishing their results in scientific journals.

To illustrate, I should like to refer to the discovery and use, in science, of heavy hydrogen. A precise physicist in California liked to calculate the exact constants of nature and to study them critically. He came to the conclusion that the atomic weights were such that hydrogen must contain a heavier isotope, probably with a mass of two instead of one. A physical chemist in New York had spent a great deal of his life in studying the properties of hydrogen and of water. He was thoroughly familiar with spectroscopy. He conceived the idea that this heavier isotope of hydrogen must exist in quantities too small to detect, but that continued fractional distillation of hydrogen would produce a concentration. He joined forces with a physicist at the Bureau of Standards at Washington who had developed extensive machinery for liquefying hydrogen at very low temperatures. Fractionation in this apparatus gave material with a new spectral line, faint, but unmistakably at the position where calculations showed that it should be if it had a mass of 2. A physical chemist at the Bureau of Standards conceived the idea that electrolysis of water might be a simpler way of concentrating this heavier isotope of hydrogen, and, together with the discoverer of heavy hydrogen, he started to electrolyze a large quantity of water and let it go for a few months, as a side issue. Sure enough, the residue of this electrolysis gave water of slightly increased density.

Immediately well-equipped and forceful departments of chemistry, at California and at Princeton, at Columbia and elsewhere started to electrolyze on a large scale. A communication from the California laboratory to the editor of the American Chemical Society two years ago announced that the separation could be carried very far and that pure isotopic hydrogen might be obtained. Immediately many chemists all over the world dropped their tools and started investigations in this most intriguing field.

In the meantime other investigators were helping unknowingly to advance this field. Commercial electrolysis of water for the production of hydrogen and oxygen had left residues richer in the heavy hydrogen, and these now suddenly became important. A young mining engineer from the West, with a quick mathematical mind, became interested in chemical kinetics, and he was able to visualize energy levels in molecules in the same way that he visualized topographical lines on a map. With this he was able to go far towards predicting reaction rates, and heavy hydrogen proved a fruitful field in which to apply and test these mathematical concepts. Physicists in various parts of the world had been trying to obtain higher and higher voltages in order to smash atoms. Heavy hydrogen gave a new projectile by means of which this smashing could be effected. And now in several laboratories one can actually see and hear the individual atoms as they are transmuted in accordance with the ancient dream of the alchemist. Chemists are attacking the problem of reaction mechanism along new lines, for they can now label the hydrogen atom and follow it through various reactions.

Looking back on this three-year development of heavy hydrogen, my claim is that no one could have had the wisdom to direct research along these different lines in such a way as to produce better results. Each of these different contributors to scientific research was impelled only by his interest and enthusiasm in creative work, and any regimentation would have been fatal. We must not interfere with our scientists. We must not starve them nor frighten them, for the progress of the world depends upon them. Research in science has been one of the few outstanding successes in the human race, and we need not less, but more of it.

SCIENTIFIC EVENTS

THE ELECTROSTATIC GENERATOR AT THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

ADVANCES in the development of electrostatic generators and the application of high voltage direct current electricity at the Massachusetts Institute of Technology were announced on May 23 by Dr. Karl T. Compton, president of the institute, at a meeting of the board of directors of the Research Corporation in New York.

The giant electrostatic generator built at the research station of the institute on the estate of Colonel E. H. R. Green at Round Hill, Mass., by Dr. Robert J. Van de Graaff and his associates, Dr. Lester Van Atta and Dr. Chester Van Atta, has been equipped with accurate voltage and current controls as well as vibration eliminators. It is now ready for the vacuum discharge tube, in which experiments in atomic disintegration are expected to begin this year. The generator develops approximately 7,000,000 volts, one of the limitations on higher voltage being flash-over to the roof of the airship dock in which it stands.

During the past year the Round Hill research staff has been engaged principally on the design and construction of the vacuum discharge tube now being prepared for operation by the generator. Much of the progress of the past year has been made possible by grants from the Research Corporation. During the coming year this vacuum tube unit will be employed in a series of experiments on nuclear disintegration in the lower voltage range, while the other additional units of the tube, which will permit extension of the experiments to higher voltage ranges, are under construction.

In the laboratories of the institute at Cambridge, under the supervision of Professor Van de Graaff and Dr. John G. Trump, attention has been concentrated on the ability of a vacuum to sustain high voltages.