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PHYSICAL AND CHEMICAL ASPECTS OF

BASIC MECHANISMS IN RADIOBIOLOGY

Editors:

John L. Magee
Martin D. Kamen
Robert L. Platzman

Division of Physical Sciences

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BASIC MECHANISMS IN RADIOBIOLOGY

II. PHYSICAL AND CHEMICAL ASPECTS

Proceedings of an Informal Conference
Held at Highland Park, Illinois, May 7-9, 1953

Editorial Committee	Conference Committee
John L. Magee	Howard J. Curtis
Martin D. Kamen	John L. Magee
Robert L. Platzman	Harvey M. Patt
	Cornelius A. Tobias

Subcommittee on Radiobiology
Committee on Nuclear Science
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PARTICIPANTS

AUGUSTINE O. ALLEN
Brookhaven National Laboratory

JOHN W. BOAG
National Bureau of Standards

MILTON BURTON
University of Notre Dame

JOSEPH S. BUTTS
U. S. Atomic Energy Commission

HOWARD J. CURTIS
Brookhaven National Laboratory

G. FAILLA
Columbia University

U. FANO
National Bureau of Standards

HYMER L. FRIEDELL
Western Reserve University

WARREN M. GARRISON
University of California

CLARENCE J. HOCHANADEL
Oak Ridge National Laboratory

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State University of Florida

HENRY LINSCHITZ
Syracuse University

JOHN L. MAGEE
University of Notre Dame

DANIEL MAZIA
University of California

LARS ONSAGER
Yale University

HARVEY M. PATT
Argonne National Laboratory

ROBERT L. PLATZMAN
Purdue University

ERNEST C. POLLARD
Yale University

CORNELIUS A. TOBIAS
University of California

RAYMOND E. ZIRKLE
University of Chicago

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National Research Council

FOREWORD

The study of radiobiology demands the integration of many areas of thought in physics, chemistry, and biology. Our academic disciplines are so compartmented that it is often difficult for investigators working on one phase of a problem in radiobiology to know about the important events occurring in other phases. It is in an attempt to overcome this difficulty in communication that the National Research Council, Committee on Nuclear Science, Subcommittee on Radiobiology, has thus far organized three conferences. The first was a symposium on radiobiology held at Oberlin College, June 14-18, 1950. It consisted of a series of formal papers and formal discussions; these were published in 1953 ("Symposium on Radiobiology", J. J. Nickson, ed., John Wiley and Sons, New York, 1952). The second was a highly informal conference held in Highland Park, Illinois, May 31-June 2, 1951, the proceedings of which were not published. This volume is an abridged transcript of the third conference. All three of these conferences have brought together physicists, chemists and biologists to discuss not their own special problems, but the interaction of radiation and biological systems in its basic aspects.

The current conference addressed itself to a question of cardinal importance in the understanding of radiobiology, namely, the nature of the mechanisms involved in the early stages of the interaction of radiation and biological systems. There was no attempt to make the discussions, comprehensive; but rather topics of current interest were discussed and analysed.

The conference committee is deeply appreciative of the efforts of Dr. Hymer L. Friedell, Chairman of the subcommittee on Radiobiology, of Dr. L. F. Curtiss, Chairman of the Committee on Nuclear Science, and of Dr. R. C. Gibbs, Chairman of the Division of Physical Sciences of the National Research Council, who gave much advice and encouragement in the planning of the conference and in the publication of this report. The subcommittee also acknowledges with appreciation the support of the conference by the Atomic Energy Commission and the Office of Naval Research through contracts with the National Academy of Sciences.

For the Committee

Howard J. Curtis, Chairman

John L. Magee

Harvey M. Patt

Cornelius A. Tobias

PREFACE

This volume was prepared from the transcript of an informal conference held in Highland Park, Illinois, May 7-9, 1953. The participants speculated freely and subjected their ideas to the give and take of a lively discussion, and many of the ideas put forth will undoubtedly require considerable modification in retrospect. It is our hope that the reader of this volume may be able to gain some insight into the ways in which at least a small group of scientists are thinking about current problems in the basic physical and chemical phenomena responsible for radiobiological effects.

The work of the participants, as well as that of many investigators not present, was quoted freely, whether available in published form or not. It must be emphasized, therefore, that no material in this report should be referred to without specific permission of, or consultation with, the authors quoted.

Each chapter consists of a discussion prefaced by a more or less formal review of salient facts and ideas, centering around a particular topic and presented by a principal essayist. These discussions are interspersed and followed by informal comments from all participants.

A bibliography is provided at the end of each chapter which, although incomplete, should be adequate to enable the reader to pursue further any topic in which his interest is aroused.

The transcript, as originally prepared, required considerable editing in the interests of coherence. Despite the heroic efforts of the stenotypist, a large number of unintelligible colloquies were found. The deletion of such sections, coupled with the necessity of achieving continuity where none existed, has resulted in a regretable loss of some of the original flavor of the meeting. Nevertheless, we hope that an adequate compromise between historical accuracy and intelligibility has been achieved.

Finally, we should like to thank the many who have helped prepare this report, and particularly the participants in the Conference, and Mrs. Antreen Pfau who prepared the subject index for this volume. One of us (J. L. M.) would like especially to thank his wife and Prof. Milton Burton.

John L. Magee, Chairman

Martin Kamen

Robert L. Platzman

CONTENTS

INITIAL ENERGY TRANSFER FROM INCIDENT RADIATION TO MATTER

Robert L. Platzman

For this first session I have comparatively little to say. And the word "informal" in the title of this Conference will be taken very literally -- in my adherence to the topic of this morning, at least.

This topic is the one about which we know more, I think, then about any other of the topics listed, and it is the one, the vagaries of which cause us the least concern; therefore, it is actually of somewhat less urgency to us at the moment. Since we have very little time this morning, I propose to give just a brief resume of the general progress, which is likely to be of interest in radiobiology, in the general field of study of the penetration of high-energy particles through matter, and allow some time for those of you who have items of special interest to introduce to do so. This, then, will be an attempt to list a few of the very high points, with only a few moments devoted to each item. I shall cover approximately the past three years -- that is, the period which has elapsed since the Oberlin Symposium, when many of these topics were reviewed from the standpoint of radiobiology. It may be worth mentioning that such a procedure automatically omits topics of great importance which are poorly understood, if they have not been studied recently. An example is the vital problem of the energy distribution of secondary electrons.

First I might mention the experimental facilities that have recently become available. The most sensational new facility is the high-energy cyclotron ("synchro-" or "FM" cyclotron), which has given us, for example, protons of energy up to four hundred Mev. And potentially the most important, in my opinion, is the facility which provides intense sources of ions of high energy-- heavy ions bearing high charge. The two places, of which I am aware, that have such sources now are Birmingham, England, and Berkeley, California. From both of them there have recently appeared brief notes (1), (2) giving an idea of the type of ions accelerated, the currents available, and the sort of experiments performed thus far, or contemplated. I think that this work holds promise of providing extremely helpful information. The work with the high-energy cyclotron is perhaps somewhat less interesting to us, although of the greatest importance in physics, of course.

In addition we now have a variety of sources of electrons of extremely great energy. An importance of these sources to fundamental radiobiology is, however, rather unlikely.

Next let us turn to the progress in understanding of the basic parameter measuring penetration -- the stopping power. I have about a half-dozen items listed under this. In theory, in the first place, there has been some progress made by the major contributor to this field, Bethe, and a few of his students, chiefly Walske (3), (4), (5), (6). They continue to interpret stopping power essentially in terms of the individual electrons of the atom. Work in this field has recently become less active because, paradoxically enough, interest in the subject has slackened.

A very interesting paper by Lindhard and Scharff (7) in Copenhagen will appear shortly. It presents a rather different approach to the theory of the stopping power, departing from that adopted by Bethe and his school and considering not individual electrons, but the electrons in the atom as a whole, using a Thomas-Fermi model with appropriate modification where demanded. This approach, I think, should be quite useful in some areas, although in radiobiology, because of the peculiarity that we are concerned, chiefly, with atoms of low atomic number, it probably will not be very relevant. Another analysis of conventional stopping-power theory has been published by Neufeld (8).

There has been little experimental work in the last few years on stopping power at high energies. Since the first burst of enthusiasm over the high-energy protons at Berkeley (cf. the work of Bakker and Segrè (9) and Mather and Segrè (10)) very little, as far as I know, has been done with them, in the present connection. I think that the reason can be attributed to the shift of interest among physicists from penetration of radiations through foils and gases, the old-fashioned type of absorber, to the one which is of chief interest at the present time -- and a nasty one it is -- namely, the photographic emulsion. Thus it appears that physicists are experiencing some of the difficulties that radiobiologists have long known, in working with a highly complex medium.

A good deal of experimental work has been done on the effect of the nature of the medium on stopping power at relativistic velocity (Fermi effect). I might mention in concluding this section that the problem of a possible great anomaly in the stopping power of liquid water is apparently still unresolved.

FANO: Do you know about Thompson's work (11) on the effect of chemical binding on stopping power?

PLATZMAN: I have heard of this work, but have not yet seen the results.

TOBIAS: I have a copy of the report here.

PLATZMAN: When I have finished, perhaps you would give us a brief summary of it. This work is at high energy, is it not?

TOBIAS: Yes.

PLATZMAN: The third topic which I shall discuss is the process of charge exchange in the impact of two atomic or molecular systems. In recent years a good deal of experimental work, and also some theory, have been devoted to this topic. Much of this was summarized at the symposium which took place at the University of Notre Dame in June, 1952 and has now been published in the Journal of Physical Chemistry (12). In addition, there have appeared numerous papers distributed through the journals, chiefly of physics.

This is a subject which is not yet of great applicability in radiobiology, but I venture to predict that in years to come, when we know more about the basic processes, we shall have much use for this information. The physical problem is very difficult, both experimentally, where there are any number of complications, and theoretically, where the problem is extraordinarily difficult. Still a good deal of progress has been made, and as chief among the contributions I might mention the work accomplished by Allison and a number of his students at Chicago during the past few years. For instance, one of their most recent papers (13) treats the phenomena of capture and loss of orbital electrons by helium ions as they pass through various gases. In previous years several similar studies for hydrogen ions were completed (14), (15), (16). This group of investigations really appears to polish off the experimental problem -- a problem, of about forty years' standing, the literature of which had been marked by a staggering amount of discordance. We now have at least empirical knowledge of all of the main features of the phenomena which have been studied. It is truly beautiful work.

The fourth topic -- and we are gradually moving, with this point, at least, to items of more immediate interest in radiobiology -- I have arbitrarily called the phenomena of low energy: the behavior, in passing through matter, of particles, the velocity of which is not great enough to permit the application of simple theories -- e.g., the Born approximation. Here we have what I consider to be one of the two major advances in the experimental investigation of penetration phenomena of interest to radiobiology. This is the work carried out at the California Institute of Technology with Lauritsen's electrostatic generators: the study of the loss of energy of beams of hydrogen ions passing through gases at low pressure. So far there has not been a detailed publication but one will appear shortly (17). An abstract of a paper presented at a meeting of the American Physical Society has already been published, and I have some of the data here.

The experiments were performed by Reynolds, Dunbar, Wenzel, and Whaling, and involved measurement of the stopping power for protons of energy between 0.6 Mev and 0.03 Mev in a remarkable variety of gases. In this low-energy region, precise stopping-power data were previously virtually unavailable. These workers found, for instance, that the Bragg rule, about which we all have heard a great deal of discussion, is satisfied, within an uncertainty of several per cent, for proton energies between 600 and 150 kev, with the important exception of the case of NO, a notorious case because the molecule contains an odd electron. Here, just as anticipated from theoretical considerations, there is a departure from the Bragg-rule prediction of about 4 per cent. For energies below 150 kev, all compounds show departures from the predictions of the Bragg rule; these may be as great as 10 per cent. This energy region is quite obviously of great importance in radiobiology. It is extremely important, for instance, for experiments on the effects of "fast" neutrons, which manifest themselves in tissue chiefly through proton recoils.

Similar experiments, in substantially the same energy region, for just a few gases but with several different kinds of penetrating ions, have been carried out in Chicago (18). It is highly satisfying that, for protons in air, the results of the two laboratories are in splendid agreement. Several other investigators have also studied these phenomena recently.

Although the primary absorption of electromagnetic radiation is of no direct fundamental interest to us in the present conference, I may just mention the enormous practical help provided by the recent compilations of X ray and gamma ray absorption coefficients by White, at the National Bureau of Standards (19), and by Davisson and Evans, at M.I.T. (20). The latter is already published, and the former will be shortly, I understand. These studies constitute a remarkable improvement in the status of aggregate information on this topic. In addition, Dr. Fano's attention to the problems of diffusion and attenuation of gamma ray beams continues.

I have, finally, a number of miscellaneous topics. Because the physics of the penetration of high-energy radiation through matter has usually been undertaken as a by-product to more pressing problems, or, at any rate, problems that the physicists considered more pressing, we have had to look for progress in all sorts of strange and unexpected ways. One of the advantages we have recently injoyed is a good deal of study of the penetration of many sorts of radiation, of low, intermediate, and high energy, through certain types of organic compounds useful as solid or liquid scintillant materials. This, I think, has already contributed a good deal to our understanding of the penetration of high-energy radiation through condensed materials, and will without doubt contribute much more in the future.

Similar to this one is a second category, which I have already mentioned, namely, the penetration of radiation through photographic emulsions. This presents many vexing problems, and only modest progress has thus far been made.

I have saved for the last in this group of miscellaneous topics the work which I consider to be the second of the two experimental projects most important for radiobiology that have been performed in the past few years. This is the work by Jesse, at the Argonne National Laboratory, on the inonization of gases. Jesse has devoted his meticulous experimental skill to this problem for a number of years, and the results have been outstanding.

A few physicists -- not by any means a majority of them -- have been suspicious for years of the validity of many of the experimental results on the average energy required by high-energy radiation to form ion pairs in gases. Some take every experimental result literally, including the third, fourth, or fifth decimal place; others are often skeptical of the second. Jesse has made a study of ionization in a variety of gases by single alpha particles; there is, of course, no reason to doubt that his results have completely general validity, in that the physical mechanisms they reveal are applicable to any sort of high-energy radiation. He has found that many of the values in the literature are wrong, not in the fourth or fifth decimal place, but in the first or second. For example, he finds that the total ionization in the rare gases is enormously sensitive to very slight traces of impurities. To take the most striking case, helium, which has been variously reported to have a value for W, the mean energy per ion pair, of some 26 or 27 electron volts (ev), turns out, if it is pure, to have a value of about 43 ev (21).

I might mention in passing that this is interesting confirmation of Dr. Fano's approximate theory of W. When he attacked this problem a number of years ago (22), his theory gave 38 ev, whereas the experimental value at that time was about 26 ev. Now it is 43 ev, which shows, at least, that his theory was a little better than experiment at that time. We still do not have an accurate theory for W in any substance.

Jesse has studied ionization, not only in the rare gases, but in a number of other inorganic and organic gases as well.

Generally speaking, the sensitivity of the ionization to impurities arises from the formation of excited atoms or molecules which can produce an ion pair in an impact with an impurity molecule having a sufficiently low ionization potential. This effect has been studied for a variety of gases, impurities, and relative concentrations of the two. In the case of helium, for example, the mechanism is the formation of metastable excited helium atoms, which are able to ionize any impurity with great probability. Indeed, the value of W for any mixture is a function of concentration of the impurity and, at least approximately, follows the Stern-Volmer relationship (23), as it should if the aforementioned mechanism is operative.

I might mention another interesting result of Jesse's studies. Although the concentration of impurity required to reduce W to approximately its lowest value varies somewhat from one impurity to another (corresponding to different cross sections for the ionization process), the minimum value of W is more or less independent of the nature of the impurity, even for polyatomic impurities. This is in accord with the theoretical expectation that, in the impact of a metastable excited atom and a molecule, molecular processes such as dissociation of the latter are much less probable than ionization, because ionization, if it is energetically possible, is a case of "exact resonance".

The effect of impurities on the total ionization should be observable not only in helium, but also in other gases. Jesse has actually found an effect in admixtures of CO_2 with argon. This suggests that normal excited molecules -- that is excited molecules of normal lifetime (in this case, argon) -- can contribute to the ionization of the proper impurity (CO_2) is present in the proper concentration. This is because the ionization potential of CO_2 is greater than the excitation energy of argon metastables. Of course, in the case of normal excited molecules the concentration of impurity, at normal pressures, must be of the order of magnitude of a per cent. Further, if the (directly) excited molecules can dissociate, this process will be competitive with the collisional ionization. However, in the case of metastables, because of their longer lifetime, only hundredths of a per cent are required to change the value of W.

All this has a strong moral in radiobiology, and it is one which even the physicist has often taken too lightly -- namely, that one really knows virtually nothing about the value of W to apply for tissue. Even with a wholesale amount of grains of salt, it seems highly doubtful that this quantity has any present significance in radiobiology.

FANO: Thus far I know that the rare gases can be changed a lot. Has any other substance been changed by a comparable amount?

PLATZMAN: The necessary experiments have not yet been undertaken. For a large effect it will be necessary to find a gas in which metastables are produced abundantly by the ionizing radiation, and for which the excitation energy of the metastable state exceeds the ionization potential of some convenient impurity.

BURTON: Are there any substantial changes in energies per ion pair for organic compounds? You know, we usually assume that they are somewhere around 25 to 28 ev.

PLATZMAN: Such measurements have not yet been made. Of course the situation which I have been describing is ripe for detailed theoretical interpretation. The basic explanation is that which I have mentioned, namely, ionization of impurities by metastable excited atoms (and perhaps by ordinary excited atoms or molecules in some cases). Thus far, air has not been studied, in part because air forms negative ions which interfere with the measurements. Incidentally, additional suspicion of the conventionally adopted value of W for air is aroused by some recent measurements in Japan (24) of the Bragg curve of alpha particles in air, which indicate that previous investigators often did not achieve the necessary saturation of current. This was demonstrated by working at very great electric field strengths, at which modification of the Bragg curve was noted.

KASHA: Why did you exclude metastable states in the case of other molecules?

PLATZMAN: I did not mean to infer that there are not any. But there is at least one case which has been studied in which the concentration of the impurity necessary to discharge the excited atom is much greater, indicating a shorter lifetime for the latter. However, this part of the work has been only little developed.

BURTON: In organic molecules there would probably be some very low-lying metastable states, but they would not give ionization.

KASHA: That is the point. In fact, we will discuss this after Dr. Linschitz's talk. Metastable states are more readily excited in larger molecules than in rare gase atoms, but as Dr. Burton indicates, the energy would be insufficient for ionization.

PLATZMAN: Mercury has a comparatively low ionization potential, and, since mercury is a very common impurity, the implications of its possible presence should be one of the grains of salt added to the interpretation of all older measurements of W.

That is all I had planned to say, and although we do not have very much time for discussion, I hope that Dr. Pollard and Dr. Fano will contribute remarks -- and also, of course, anyone else who wishes to do so.

POLLARD: The remarks that I have to make might perhaps fit in a little better this afternoon, if you are going to discuss the actual length of tracks of low energy electrons then. But what I wanted to point out was that we have a line of low voltage work in which the voltage of the electrons varies from zero to 5000, and we use these for bombarding bacterial spores, bacterial virus, and viruses in general, and making measurements on the surface area as measured by the loss of infectivity of the material and also loss of the serological combining power.

In the course of this it became very necessary to know the range of electrons in the kind of material we were working with and, as you point out, the theory is very poor down there. This is where the Born approximation doesn't hold too well. So we looked for a way by which we could make a sure measurement of the range of low voltage electrons in biological material. What we did was to take essentially a very thick enzyme layer on a plate, to be precise, and simply burn off with a complete bombardment as much of the enzymes as the particular energy would take. That is to say, the experiment consists of putting down a layer of enzyme, known in amount by the way in which it is pipetted there. Then you expose it to long-time bombardment of electrons of different energies. Then you assay it. If very low voltage electrons are used you get a rather interesting result. A monomolecular layer of invertase is inactivated. As you increase the energy of the electron this same picture continues until you pass through the molecule, and this occurs with an energy of about 150 electron volts. Thereafter you start to go up and you should go up in steps, but the steps get blotted out and the result is one can get an estimate of the thickness of the material traversed from about 300 to about 2000 electron volts. This lies a little lower than Lea's theoretical curve. But it follows it quite well, and this represents, therefore, experimental data on the way in which energy is lost.

FANO: This is the practical range, so it is bound to be lower than Lea's figure which was meant to be the true range.

POLLARD: That is right. It is the range with scattering.

FANO: I think Lea's values were even lower, if I remember right, as compared with other averages.

POLLARD: They probably would be, because ours are not much lower, and the scattering would certainly introduce at least, let's say, a 40 per cent change. That is putting it pretty roughly.

FRIEDELL: What was this enzyme?

POLLARD: Solid invertase.

BURTON: How low could you go in electron energy?

POLLARD: The lowest effective energy is one volt.

BURTON: Could you actually work with energies so low?

POLLARD: Yes, in order to work with one volt you have to work with monolayers, and this has been done by Hutchinson who really is in charge of this work. If you study the action on a monolayer of bovine serum, as measured by the Rothen technique in combination with the specific antibody, you can detect an effect of one electron volt.

PLATZMAN: How do you avoid electrostatic effects?

POLLARD: I am not too sure except I know they are taken care of. It is not simple. Most of the precautions that have to be taken in these things were found necessary and were taken. In other words, a lot of inconsistencies occurred until proper grids and adequate grounding and proper conductivity of the surface were secured, but once these things were done, it is pretty clear that you can get effects down to one volt which is rather interesting. They need very large amounts of electrons.

BURTON: How closely do you fix that one volt?

POLLARD: To about 30 per cent. So you might say it is from 0.85 to 1.15 ev.

KAMEN: You said there were some energy values for which there was very little inactivation.

POLLARD: If you are referring to bacterial virus, you measure the thickness of the skin.

KAMEN: This, I believe, was with enzymes. There was a certain energy at which you got no inactivation.

POLLARD: Yes. Well, with the preparation we use, if you are bombarding an enzyme, not a monolayer, then there certainly is a dirt layer of some kind. No matter how pure the enzyme, you will have some impurity in the material on the surface. We have not been able to carry out any really low voltage work except with monolayers.

KAMEN: As far as you know, any energy whatever would have an effect?

POLLARD: Not below one volt. Below one volt apparently the effect really does die down.

BURTON: The important point is that you believe that you have established that a one-volt electron has produced an effect.

POLLARD: It must be stressed that the cross section for this process of one volt is very, very small, and in order to get somewhere near the ordinary cross section which is associated with ionizing radiation, the energy has to be much higher. Of the order of 5 to 20 volts. In that range. It is still going up very quickly.

BURTON: Will you have a word to say about why cross sections for one-volt processes are so small? Do you think that the cross section is really very small or that the finding is merely a reflection of your method of measurement?

POLLARD: I think this is a secondary process of some kind.

BURTON: Do you mean that something superimposed, like an electrostatic effect is involved?

POLLARD: I don't think it is that. No, I think there is a low energy method of inactivation which is very inefficient.

MAGEE: Like electron capture?

POLLARD: It might be something like that. It is analogous to heat, but it is not the same as heat. For instance, it is possible to calculate the heating of these specimens, and we have thermal inactivation data very accurately plotted and it can't be that. It would take about 150^{o} in the dry state. It is not heat, but it is what I personally think might be the "prepartition" effects of heat. That is to say, you have there a fairly large number of excitations in the order of one electron volt, which you don't normally get in the thermal case, and the multiplicity of these, many of them present one after the other, gives the effect.

CURTIS: In the case of your heat, how high does the energy run?

POLLARD: Well, that is a hard one to answer. ΔH is the same as ΔF in this case, and it runs about 1.2 ev. But while that fits very nicely with this figure, I want to hurry to say that I am not at all sure that that is a very statistical piece of information, and, while it might apply to the very lowest possible binding practical, it still is very hard to interpret it. That figure is a great big average figure.

CURTIS: But it is a nice order of magnitude.

POLLARD: The two go together. If you try infrared, you don't seem to get any effect.

BURTON: Bond rupture is not necessarily involved. Why not a rearrangement? It can be produced with much lower activation energy.

POLLARD: I was merely taking the ion theory of the activated state literally, and this is passage over a hump of some kind.

BURTON: However, such passage could involve a rearrangement, rather than a rupture.

POLLARD: Yes, certainly.

LINSCHITZ: Are you really satisfied that the high energy tail of the distribution has been cut down?

POLLARD: Yes, about that we are satisfied. That is all right. I am not able to state the precautions about electrostatic effects here, but I am satisfied they are all right. However, you have to take my word for that.

KASHA: Could it be possible that you are just successively populating several vibrational states in the molecule under steady-state electron irradiation?

POLLARD: Yes.

KASHA: In other words, this should be possible to duplicate with infrared irradiation, if you have sufficiently high intensity.

POLLARD: That is what we feel should be done.

BURTON: As a matter of fact, we have a situation in a field rather remote from the one under discussion, corresponding exactly to your model. I refer to chemical reactions in an electrical discharge through methane. In that case we apparently have important successive excitation effects. The primary excitation process produces a species which is in turn excited by electron impact. Without such secondary excitation, methane could be re-formed or ethane would be produced. If the secondary excitation process occurs, acetylene is produced. This total process is similar to what you are talking about.

KASHA: It has been possible to study infrared emission in molecules, and, if this were the mechanism, you would definitely observe it while the electrons were bombarding the molecules. I think Plyler (25) has published some infrared emission spectra of molecules, around one volt.

POLLARD: That would be a hard job for us to do.

ONSAGER: If it were a matter of successive effects, then the inactivation should increase with some power of the amount of time of bombardment.

POLLARD: There should be a wavelength effect.

BURTON: I do not agree with Dr. Onsager. Not the time of bombardment, but the intensity of the bombardment is important. That is precisely what we found. We found the so-called "rate constant" to increase as a function of the intensity.

ONSAGER: I might volunteer another suggestion here, that with one-volt electrons it still isn't certain that the total energy available is merely one volt, because when the electrons end, whatever material we are working with, they are accelerated by the contact potential. At least I think they will be attracted. The contact potential is not very well known and even difficult to define, but we have to allow for it. It depends on the structure of the surface layer.

BURTON: How much do you think the total energy might be?

ONSAGER: A couple of volts.

BURTON: That is an interesting figure. It is just of the right order of magnitude for some forbidden transitions; for example to triplet states, which might lead to chemical reaction.

KAMEN: What are the energies of the electrons in an electric discharge?

BURTON: I felt that question coming. Although one always thinks of an electrical discharge process as being very violent, it turns out that the energies of the electrons are for the most part of the order of 2 ev or less. This means that the temperature turns out to be rather small. Of course, in the particular case discussed, there was a very non-Maxwellian distribution of energy, apparently because of the turbulent conditions of discharge. In such case there is perhaps a long high-voltage tail, but the low-voltage electrons in non-Maxwellian distribution predominate. There are enough such electrons to excite very low-lying states to an important extent. In the work I mentioned, the first step corresponding to Dr. Kasha's suggestion was conversion of methane to methyl. Methyl turns out, in our opinion, to have a carbon-hydrogen bond dissociation energy a little lower than that in methane. The significant state, in this case quadruplet, is consequently also a little lower. Thus, the second activation leads directly to decomposition of the methyl itself. In other words, successive excitations are necessary for the effect observed. Without sufficient energy, only methane is observed. The methyl won't be excited, and there will be no product of its decomposition.

ONSAGER: It combines with other methane?

BURTON: No, not under these conditions. The cross section for the low-voltage excitation process appears so high that methyl is substantially removed very quickly. The importance of such an effect can be seen from two calculations from formulas for non-Maxwellian distributions: the Townsend approximation and the Morse approximation. The steady state concentration of CH_3 at an assumed electron temperature of 0.5 ev and an assumed C-H bond strength difference of 0.3 ev is less than 10^{-19} that of CH_4. (26)

ONSAGER: With what does methyl combine?

BURTON: Ordinarily, if you let it wait around long enough, it will react with hydrogen and give you methane under these conditions, but in an electric discharge it yields CH_2, a rather stable radical. The triplet state in CH_2 seems to be higher than that in methane.

ONSAGER: But suppose the intensity is low. Then the CH_3 back reacts back with hydrogen?

BURTON: Well, I cannot talk from my own work because I have not done this. Other people have done experiments at low pressure and have obtained considerable amounts of ethane -- but I suspect more back reaction such as you suggest than anything else.

LINSCHITZ: What would be the dose rate in these experiments you speak of, relative to the dose rate in the electron bombardment of the enzyme films?

BURTON: There is no way of comparing them. I just don't know what their dose rates are. Undoubtedly, the dose rate may be very much higher in their experiments.

LINSCHITZ: Also the rate of deactivation of the molecule in the gas would be much less than that of an excited molecule in a solid, so that for both these reasons I think a multiple excitation process is rather unlikely.

BURTON: All I did was to give an experimental situation that corresponded to the model suggested by Dr. Kasha. For a parallel situation in a condensed system there would have to be some very strict selection rules forbidding the deactivation transition.

PLATZMAN: May I return the discussion to the subject for this morning, and ask Dr. Tobias if he would care to speak now?

TOBIAS: Theos Jardin Thompson, working with Segrè and Chamberlain, wrote a recent Ph. D. thesis on the effect of chemical structure on stopping power (11). He studied the stopping power of 380 Mev protons with 270 Mev mean energy in various inorganic and organic compounds having different percentages of hydrogen, carbon, oxygen, nitrogen, and chlorine. He concluded that the influence of chemical binding is less than 1 per cent, that is, the elements in the various compounds have the same stopping power within one per cent. He could, however, identify small but measurable deviations from the additivity of stopping powers of elements from compounds. From his work there resulted a number of quite accurate stopping power determinations for hydrogen, which is of special interest, as well as for other elements.

POLLARD: You don't have the effective I values, do you?

TOBIAS: Thompson gives the relative molal stopping powers (S) with respect to copper and the mean ionization potential, I. Some of his values are listed in table I.

TABLE I

RELATIVE STOPPING POWER AND MEAN IONIZATION POTENTIAL OF VARIOUS ATOMS

Element		S	I
Hydrogen	(molecular)	0.0472 ± 0.0002 (est.)	18.2 ev
Carbon	(graphite)	0.2455 ± 0.0005 (est.)	70.2 ev
Nitrogen	(molecular)	0.2837 ± 0.0001 (est.)	76.3 ev
Oxygen	(molecular)	0.3188 ± 0.0003 (est.)	88.3 ev
Chlorine	(from compounds)	0.6335 ± 0.0035	153.7 ev

FANO: I have this only by word of mouth. The striking thing was that from the value of effective I you could really say how many double bonds there were in a molecule.

PLATZMAN: That contradicts the statement that the effect of chemical binding is negligible.

FANO: The experiments are accurate within a very small fraction of one per cent; and that is the striking thing, that one per cent effects could be detected.

PLATZMAN: Dr. Fano mentioned a remarkable precision. Was any great advance made since the experiments of Mather?

TOBIAS: I think the chief experimental advance was in the technique of ionization measurements. The problem is to measure the ratio of ionizations at two different points in the Bragg curve. This is done with two ionization chambers. A number of combinations of absorbers are placed between the two ion chambers. Now it is difficult to obtain the two ionization measurements since the proton beam shows considerable intensity fluctuations. Thompson built a ratio meter, an instrument which measures the ratio of ionizations in two ion chambers instead of the actual values. The ratio is independent of beam fluctuations. He could also make measurements with several combinations of absorbers without shutting the beam off.

BOAG: Thompson claims accuracy of the order of 0.1 per cent, and demonstrates that the stopping power of compound molecules can be calculated with an error much less than one per cent from the atomic stopping powers of the constituent atoms, provided different values are assigned to the stopping power of H in saturated and unsaturated compounds, and some similar allowances made for the type of chemical binding of other light elements.

PLATZMAN: The percentage deviation from the Bragg rule is smaller at high energy, of course.

FANO: Yes.

PLATZMAN: The point is that if there were a deviation from the Bragg rule of one per cent at very high energy, it would be considerably greater at low energy.

TOBIAS: A small difference detected with 340 Mev protons should become greater with say 1 Mev protons. In the latter case the experimental technique is much more difficult, however.

PLATZMAN: Did he measure the stopping power of liquid water?

BOAG: He used liquid oxygen and liquid hydrogen as well as liquid water?

TOBIAS: Yes, and also liquid nitrogen.

PLATZMAN: At least for gases, information on lower energy particles is provided by the Cal. Tech. work which I mentioned. Has Thompson compared his results with these?

TOBIAS: He did not make a comparative study. The values from Thompson's high energy work given in Table II may be of interest.

TABLE II

RELATIVE STOPPING POWER AND MEAN IONIZATION POTENTIAL OF VARIOUS ATOMS AS AFFECTED BY CHEMICAL BINDING

Element	Type of Compound	S	I
Hydrogen	Saturated	0.04797 ± 0.00007	15.5 ev
	Unsaturated	0.04879 ± 0.00010	13.0

Element	Type of Compound	S	I
Carbon	Saturated	0.24627 ± 0.00016	69.3 ev
	Unsaturated	0.24674 ± 0.00009	67.2
	Highly chlorinated	0.2509 ± 0.0008	57.9
Nitrogen	Amines, nitrates, etc.	0.2785 ± 0.0025	89.4
	Nitrogen in ring	0.2870 ± 0.0020	68.8
Oxygen	-O-	0.3187 ± 0.0024	88.5
	O=	0.3226 ± 0.0010	79.8
Chlorine	All	0.6335 ± 0.0035	153.7

ALLEN: We would like to know the energy distribution of primary events. I made some attempt to look this up a couple of years ago, and had to go back to the C.T.R. Wilson cloud chamber pictures of 1923. I wonder if anything has appeared since.

PLATZMAN: Dr. Fano has tried to find the energy distribution of the secondary events. I am sure that he will agree with me when I say that this is one of the things of which we are most in need.

FANO: It is a difficult problem.

PLATZMAN: This would be a very fine experimental project for the subcommittee to stimulate, because the work could be done, and physicists are interested in it. The same holds for the theory.

FANO: We would have liked to have done it, but our initial attempts indicated that the problem was much more difficult then we originally believed.

POLLARD: This is actually really quite important in radiobiology because we are now turning up effects in which there is a threshold energy. For instance, if a deuteron beam passes through a virus, it looks as though a certain energy has to be released in the virus to inactivate it. There is some evidence in the case of Flexner's toxin that this is so and possibly also in the case of respiratory enzymes. Unless you know the number and energy of the secondary electrons produced, you cannot compute this thing numerically. There is an important third datum, so to speak, you have to have.

Then there is the opposite extreme of this: when you get highly sensitive conditions of a molecule, which can happen, you need to know the number of excitations, because then the photon sensitivity may become high. If there is a high proportion of excitation to ionization, it may produce a notable effect, which will not be quite different because it will not necessarily require the ionizing radiation to pass through the molecule, since the photon travels over a corresponding distance and it may be further away, while the ion is localized.

TOBIAS: Has anyone in Jesse's group worked on water vapor?

PLATZMAN: No, although he is considering it. The only modern measurement of ionization in water vapor is that by Appleyard (27). It is not easy to do and I don't think it is terribly important; as a matter of fact, it might even be a misfortune if somebody measured W very accurately because then immediately most biologists would assume that liquid water would behave the same.

BURTON: We have spoken about ionization as having a different effect from excitation. I think that during the course of the discussion there may be quite a question raised as to whether the ionization is actually persistent enough so that you can say that any chemical process ensues from the ionized state itself. Instead, we might be dealing with higher excited states. Thus we must note that when we say ionization in contrast with excitation, all we are really concerned with are high energy states compared with somewhat lower ones.

POLLARD: There is the other purely empirical fact that the quantum yield is low for most of the studies of cases of excitation, whereas the ionic yield is close to 1. This is in the region, say, of 1900 Å on out. The quantum yield for most biological molecules is pretty low. In the order of 0.001 or something like that, and this would look as though it would take 1000 excitations to produce that effect.

KASHA: For inactivation ?

POLLARD: Yes.

KASHA: That would seem reasonable from the spectroscopist's point of view.

POLLARD: Then one has to blame something other than excitation.

BURTON: Dr. Pollard, the energies of the excited level could be different. After all, the phenomena produced depend also on the amount of energy available for an individual process.

ALLEN: It is also a matter of geometry.

POLLARD: We are going to check these by studies in the vacuum ultraviolet, which should give us an answer to that. We are proposing to go down to 1100 Å. There are some effects which indicate that the molecules are more sensitive in that region, but it is the whole region where physical studies are necessary.

KASHA: I should like to make a comment about a simple experiment by Ageno, of the Institute of Health in Rome, which appeared in an Italian Journal (28) and which has to do with an attempt to find out how far out the emission in a liquid scintillation counter travels. Roughly, the experiment was to take a nickel button, which was flat, and which he coated with polonium by electroplating, I believe. Of course, he knew exactly the length of the alpha-particle path. He set up a camera to photograph a picture of the scintillation (in the dark) from this button in a side view, and he found, roughly, that the emission occurred over approximately ten times the known path of the alpha particles. He carefully tested to see if diffusion of radioactive material was occurring during the experiment time. He found it was not.

ALLEN: Ten times the length, or ten times the breadth?

KASHA: Ten times the length. He concluded that it was possible in the liquid scintillation counter and that an important mechanism was one of emission of some radiations which could travel through the solution as electromagnetic radiation which would then excite the emitting molecule. This interested me very much, and I should like to say something about it later.

POLLARD: It must be high energy.

KASHA: They are probably vacuum ultraviolet frequencies, and the most unambiguous experiment might be a two-cubicle experiment in which a sapphire window between two compartments would allow high frequency electromagnetic radiation generated in one to pass into the other. A collimated primary irradiation beam could be passed through a cell containing one of the liquid scintillation solvents, e.g., benzene. The second cell could contain a scintillation solution, e.g., one of those given in Kallmann's tables (29). The photomultiplier tube could be collimated to observe only emissions from the second cell. The initial part of Kallmann's scintillation intensity versus concentration curves could be explained on the basis of a reabsorption of such intermediate radiation.

ALLEN: The feeling is that this distance is too long to be accounted for by migration of excitation?

KASHA: Yes, that would be at most something like 1000 Å, I think. The Kallmann and other experimental results indicate something like 100 Å at the most, and Kallmann thinks it is 40 or 50 Å. This experiment really seems to indicate distances beyond that.

BURTON: What is the phenomenon, induced fluorescence or simple quenching?

KASHA: You have to pick up the radiation and, therefore, to quench it.

PLATZMAN: Do you mean experiments with light?

KASHA: It is the average separation at the concentration given, and there is some doubt as to whether that means the distance for transmission of the energy. In choosing a scintillation medium, Ageno selected some of Kallmann's solute-solvent pairs.

BURTON: In the work that Franck spoke about on induced fluorescence, what is the greatest distance that he assumes the energy can travel?

PLATZMAN: What system?

BURTON: I don't know. What is the greatest distance for any system you know about?

KASHA: In solutions it is 40 or 50 Å.

BURTON: Did Ageno work on solutions?

KASHA: Yes, on liquid hydrocarbon mixtures. I think the thing that is missing from all the work on liquid scintillation counters is the high-energy spectroscopy. Which pairs work and which don't work are really quite mysterious, and yet when the spectroscopists look at the higher energy states, they certainly vary extremely between the kinds of molecules used. It could very well be that the scintillator which picks up the energy in the system may be capable of absorbing higher energy radiation to which the solvent is always partially transparent.

PLATZMAN: If the solvent is transparent, you should be able to observe the direct light with the pure solvent. Would the absorption spectrum of the solvent fall off in the far ultraviolet?

KASHA: Yes. For instance, in the case of benzene between 2000 and 500 Å, there are regions of some transparency.

PLATZMAN: Is emission in that region observed under bombardment?

KASHA: No, there is little in that region.

PLATZMAN: Are you saying that you think the luminescence dies off towards shorter wavelengths and then starts again in the ultraviolet?

KASHA: No, I would say that the secondary electrons may cause the emission of higher frequency light first, which then can be absorbed competitively by the solvent and the solutes. The solutes re-emit this absorbed high-frequency radiation.

PLATZMAN: How do the electrons cause this high-frequency emission?

KASHA: Possibly by recombination.

LINSCHITZ: One point I might make is that the absorption of such radiation may be quite inefficient because the excited states that you can reach by particle bombardment or fragment recombination need not correspond to those that might be reached by optical excitation, and that might also give regions of transparency in the solvent.

PLATZMAN: Why do you believe that the recombination transition should be radiative rather than non-radiative?

KASHA: There are radiative recombinations of molecules.

PLATZMAN: Yes, but always less probable than non-radiative ones. We are discussing neutral recombination, not positive ions and electrons. Are you not thinking of two fragments?

KASHA: Oh, yes, molecular fragments.

PLATZMAN: They would be even less likely to radiate.

ONSAGER: There is a chance that they would, nevertheless.

BURTON: What is the order of magnitude of the chance of radiation on recombination of the pair of radicals?

MAGEE: It could be up to 100 per cent, I would think. If there is enough binding energy in a particular excited state formed on association so that it will not dissociate thermally, then it has nothing to do but radiate.

LINSCHITZ: There are certain chemiluminescent reactions in which radical recombination seems to be responsible for the electronic excitation. Radiation must of course compete with thermal degradation for this energy. Relatively few chemiluminescent efficiencies have been measured, but even in the best cases the light yields are not greater than a few per cent, in condensed systems. Generally, the efficiency seems to be very much lower, particularly if complex, non-fluorescent molecules are involved.

BOAG: A year or two ago we looked for recombination radiation from water in the following rough way. A 1500-kev electron beam was allowed to pass into water contained in a quartz dish. The Cerenkov light emission was considerable and enabled a good spectrum to be photographed (on a Hilger medium quartz spectrograph with a narrow slit) in about 40 seconds. The electron energy was then reduced to below 250 kev and the same total electron current was passed into the water, but no spectrum was obtained, even with a wide slit, in one and a half hours. By reducing the energy below 250 kev the Cerenkov radiation was eliminated, but one would expect any recombination radiation to be reduced by a factor of only six. One may calculate an upper limit to the energy radiated as recombination radiation in the following way:

$$\text{Recombination radiation escaping} \lll \frac{40 \text{ secs.}}{1\frac{1}{2} \text{ hours}} \times \text{Cerenkov emission}$$

The sign $\lll$ denotes that there are extra factors for (a) wide slit vs. narrow slit and (b) no photograph vs. good photograph. Now the loss of energy of an electron in water due to Cerenkov radiation is of the order of 10 kev per cm. whereas the total rate of energy loss is about 2 Mev per cm. so the Cerenkov emission accounts for only one-half per cent. It seems that any recombination radiation in the ultraviolet or visible must be less than one per cent of the Cerenkov and thus less than 10^{-4} of the total. This applies of course only to the spectral region between 2300 and 5000 Å.

KASHA: You have to check two other things. One is -- are there any electron-excited states in the water which come in the region. That would be coveredby your question. The other is -- are there any metastable excited states. And there are none, are there, in water?

BOAG: An experiment has been reported by Dee and Richards (30) in which alpha particles impinging on a thin film of water gave a soft X radiation which passed through quartz and was detectable by a photomultiplier.

PLATZMAN: What is the present status of that work? In this country most people are skeptical of its validity.

BOAG: Richards himself did not support it very strongly at the Faraday Society discussion at Leeds. However, some American workers have recently published apparently confirmatory data, and they even gave a spectrum they had photographed. (31)

PLATZMAN: All I remember is that it was not very impressive.

BOAG: I agree.

BURTON: One could say that the most impressive evidence against it has not been published. Other people have tried to do what Richards has done and obtained negative results. For instance, Miller at Edinburgh has done some experiments.

ALLEN: Miller controlled the conditions more carefully.

BURTON: Essentially, the experiment involved a very thin smear of water on a quartz plate, on the other side of which there was a chemically sensitive system (for example, aqueous ferrous sulfate). They found that although the water layer was thick enough to stop the alpha particle, nevertheless the ferrous sulfate solution on the other side of the quartz was oxidized. That is the story. So far as I know, no one else has ever duplicated the result.

ALLEN: Miller went to great length to show first there is no chemical reaction; second, that there is no radiation transmitted.

PLATZMAN: We don't know enough to say that there is no radiation. The hard thing to believe is the intensity figure they quoted, which is comparatively great.

ALLEN: There was no radiation which could get through quartz that Miller could detect by scintillation.

PLATZMAN: Dee and Richards claimed that the amount of energy in the radiation was a substantial fraction of the incident energy. This is the point that is hard to believe. Franck has pointed out a mechanism whereby some energy may be radiated. In the alpha-particle track there is something like a plasma for a brief time, with a great charge density, and such a system is known to radiate in the far ultraviolet.

HOCHANADEL: According to Spence, Richards, who is now at Harwell, is still working on this problem of light emission and is not yet ready to retract his previously reported observations.

PLATZMAN: That is fine. I am sure we are glad to hear that. We don't know enough to say that it is wrong; it is just that if somebody comes along with a hair-raising conclusion, the burden of proof is on him. It is not on everybody else.

FANO: I might describe the state of a few programs at the Bureau of Standards to which Dr. Platzman has referred. One is the study of the absorption coefficient of gamma rays in narrow beams. It is what is usually called the absorption coefficient. The work was undertaken quite a few years ago on a somewhat more ambitious basis than the Davisson-Evans work (20), essentially to cover a much wider range. The report on this work by Miss White (19) has been circulated informally and its supply is exhausted. It is planned to put it out in the form of a circular, but some difficulties have to be settled, especially in the low energy range; to be specific, below 100 kv. and especially under 10 kv. The situation is that both theory and experiment have an uncertainty of ten or twenty per cent, which is more than I had previously thought. Miss White, after long cogitation, decided to stick to theory which, however, in the present state of art could be only essentially hydrogen-like theory. Good experimentalists, like Parratt at Cornell, to whom I have talked,did not attach more reliance to the experiments than ten or twenty per cent either. Miss White landed ten or twenty per cent lower than the experiments, as, for example, embodied in the Victoreen semi-empirical formula. The situation six months ago was regarded as open. One could see flaws in the theory, and one could see flaws in the experiments. It would be very desirable and rather difficult to improve the experiments performed some 15 or 20 years ago. At the Bureau we ran only one preliminary test on the absorption coefficient of carbon with copper R-alpha, and that fell near the Victoreen formula. So the best we can say is that White is likely to be low and Victoreen might be better. How far we will have to revise we don't know.

At higher energies, above 100 kv. the data are much more dependable, to within two or three per cent, and often, especially in light elements, much better than that -- one per cent.

This covers the narrow beam work. Much of our work has been on attempts to determine by theory the penetration and diffusion of gamma or X rays through large masses of material. The gamma ray problem we regard as essentially finished. But essentially we figure we have it in hand for all the effects where the medium can be regarded as infinite. Surface effects, which effect, of course, the lower energy scattered components particularly, we do not have well in hand. There are some beginnings. For instance, just to quote one figure, it turned out that if a million-volt photon strikes a water surface, the probability of its coming back is of the order of one-third. This is something about which, until three months ago, we had absolutely no idea whatsoever. It might have been ten or it might have been eighty per cent.

MAGEE: Is this backscattering essentially the result of the first Compton recoil?

FANO: I mean the probability of the photon going around in the water and eventually coming back out.

PLATZMAN: It is for a thick absorber.

MAGEE: This includes all backscattering to get out?

FANO: Yes. Many photons come out with low energy; on an energy basis, the average energy fraction coming out is not one-third, but only five or six percent. This is very preliminary.

MAGEE: Has each photon been scattered about three or four times?

FANO: Very often more. A few photons, one or two times. Many even ten times.

Regarding the penetration and diffusion of electrons, we are breaking the problem down into a number of partial problems and making some progress. It is the sort of thing that ought eventually to be of very considerable interest to radiobiologists because the problem of where the energy of the electrons is dissipated is a fairly wide open question, and we are going at it systematically. We don't have anything very striking to report. The main thing is to point out that this work is in progress.

PLATZMAN: There has been some new theoretical work on the photoelectric effect by Meyerott (32). Do you know about that?

FANO: On absorption coefficients? Yes, that was reported the other day in Washington.

PLATZMAN: I went over some of this ground with him, and it is shocking how little experimental material there is with which to compare it. For instance, he calculates a partial cross section for different electron shells at a wavelength at which several shells contribute to photoelectric absorption, and there have been absolutely no experiments that we could find that give the separate contributions. Again that is something that would not be hard to measure.

BURTON: If there is no other discussion of this point, I should like to return to what Dr. Boag had to say about water and what we were all talking about, particularly what Dr. Kasha was saying.

In a complicated organic system excitation to an energy state sufficiently high for dissociation is not necessarily followed by an observable chemical change. Various aspects of the Franck-Rabinowitch effects are involved. For example, a relatively small amount of energy may be tapped, leaving the molecule in a highly excited state which may persist for a long time prior to dissociation, for example by a rearrangement process. In that time, complete deactivation or many other competing processes might occur. That situation simply does not exist in water.

KASHA: Why doesn't it exist?

BURTON: You just don't have a sufficiently complicated molecule in that case. The hydrogen atoms are easily expelled so that the persistent highly excited state does not exist in this case. Thus the picture that Dr. Kasha suggested appears highly plausible in the case of organic molecules.

ALLEN: In regard to the difference between the effects of ultraviolet and ionizing radiations, the talk has been about high-energy fluorescence as an explanation. I think we should not forget the possible geometric effects. In the high energy radiation you have excitations occurring to groups very close together, and these may very well interact with each other, whereas the isolated ones you get with the ultraviolet will not.

POLLARD: That is why it is so important to know where they are.

ALLEN: Exactly.

TOBIAS: I wish to make a brief remark on the status of investigations with multiply-charged ion beams at the sixty-inch cyclotron of the University of California in Berkeley (2). Miller, Putnam and Rossi, working with Hamilton, have succeeded in obtaining a fairly intense internal carbon (6^+) beam and a moderate external beam. Miller (33) has recently completed a Ph. D. thesis, working with McMillan on reactions of fast carbon nuclei in photographic emulsions. He has considered electron exchange, and he came to the conclusion that the Bragg curve is not very much influenced by this effect. Further, Barkas (34) has made a study of a number of light ions, such as lithium, beryllium and boron, which may be obtained from nuclear transmutations. The range-energy relationship of these nuclei was evaluated near the end of their range, yielding important data for electron exchange.

PLATZMAN: What energy do the recoils have?

TOBIAS: A few Mev per nucleon. The protons producing the interaction may have as much as 340 Mev. The ions themselves are products from interactions on various elements, e.g., carbon or beryllium. They usually recoil at lower energies than the initial proton energy and are selected for momentum in a magnetic field combined with a slit system. Barkas determined the range correction in photographic emulsions due to the part of the track where electron exchange is important, and found this proportional to Z^3. Returning now to the carbon ions, perhaps it may be of interest to you that the 120-Mev carbon ions are now in use for radiobiological research. We have had experiments in which the dose rate from this beam was as high as 3000 r.e.p. per minute.

FANO: What sort of beam current do you have?

TOBIAS: The external beam current is about 3×10^{-11} amperes; the internal beam, which may be used in transmutation experiments, is more than 1000 times greater. The energy is about 120 Mev. Actually the particles are not monoenergetic, and if you wish to select a monoenergetic beam, you have to sacrifice intensity. The range of these particles in tissue is about 50 microns, so that the particles are suitable for studies on microorganisms, liquid systems, and surface layers of tissues.

FAILLA: Do you have any idea of the RBE of the carbon ions?

TOBIAS: The only organism for which sufficiently complete data are now available is the haploid yeast cell. The RBE for this organism increases with specific ionization (35), and for polonium alpha particles it is about 2.5 (when compared to X rays). In our group Ann Birge and Joseph Sayeg (36) performed carbon (6+) experiments on the same strain of cells and found that in the region of ionization which is beyond that of alpha particles $\left(-\frac{dE}{dx} > 2\cdot 10^{9}\,\mathrm{evg}^{-1}\mathrm{cm}^{2}\right)$ the RBE starts to rapidly decrease again. It is interesting to note that it takes only an average of three carbon particles to kill a single cell.

ENERGY TRANSFER FROM SECONDARY ELECTRONS TO MATTER

Robert L. Platzman

I should like to devote the opening portion of this second session to a presentation of some speculations with which I have been concerned recently, very closely related to the subject originally assigned for this part of the conference and, indeed, falling somewhere between the second and third topic -- probably right in the middle.

Those of you who were at Oberlin will perhaps recall that at that time I expressed the idea that those who devoted consideration to problems involving so-called basic mechanisms in radiobiology, very definitely including myself, were working in what might well be called a fool's paradise. This afternoon I should like to lead you briefly into the nether world, in an attempt to be realistic about some of these problems, for it is in the nether world, you will recall, that most of the intellectual treasures are to be found.

I wish to make it quite clear that the path along which I shall lead you is not likely to be -- indeed, is probably not the correct one. But of one thing I am quite certain, and that is that some of the scenery I shall point out to you is authentic.

When high-energy radiation interacts with matter, the sequence of events which ensue may be divided into three general stages.

First there are produced a number of excited atoms or molecules, positive ions, and swiftly moving electrons. The number of electrons multiplies for a brief time, their energy, on the average, decreasing, and at the end of what I shall call the first stage there are present in the medium a certain number of excited atoms and molecules of various types, a certain number of positive ions of various types, and a number (equal to the number of positive ions) of electrons, all having energy lower than the lowest electronic excitation potential of the medium. The energy distribution of the electrons at this stage is still largely unknown; most of the electrons have an energy of the order of 1 to 5 electron volts.

During this first stage the interaction of the radiation -- primary and secondary -- is dominantly with electronic systems of atoms and molecules, and at the end of this stage comparatively little of the absorbed energy has been converted into heat.

The second stage I shall call that in which the electronic kinetic energy is further degraded to thermal energy, and during this period, since the electrons can no longer communicate energy to electronic systems, because of the energy requirement, their interactions must be with atomic motions of various types. Hence, all of this energy loss goes into heat (1).

Finally, at the end of the second stage, we are where chemistry can take over, because there then follow various thermal reactions (constituting a third stage), some of known and many of largely unknown types but still definitely the familiar chemical reactions considered by the chemist, with, of course, the well-known complexity that the spatial distributions are not homogeneous as in ordinary chemical reactions or even as in most photochemical reactions. The problem of these heterogeneities has received very little serious attention; Dr. Magee in particular, has pioneered in the field. I think that we can look for a good deal of progress on this point in the coming years.

This afternoon I shall discuss just the second stage, namely, the degradation of kinetic energy of electrons having energy too low to excite electronic systems. For simplicity I should like to consider a single electron interacting with liquid water. This idealized problem should be immediately applicable to radiobiology. I might mention in passing that when this problem of the loss of energy by secondary electrons is mentioned or treated at all in the literature, it is almost always treated incorrectly. For instance, the statement is commonly encountered that electrons lose energy in elastic collisions, in packets of thermal size, etc. This is incorrect.

Let us start by considering the various types of interaction of a rather slow electron with the medium. First I shall outline these various types and what we know or do not know about them. Then I shall try to construct a picture of the actual moderation of electron kinetic energy from the lowest electronic excitation potential down to thermal energy. Finally, inquiry will be made into the fate of the thermalized electron.

The types of interaction of an electron of energy of a few electron volts with liquid water are three. First, it may interact with the oscillations of the medium -- the atomic oscillations. The electronic oscillations are excluded by energy conservation. Second, it may interact with the "dipolar structure" of the medium. And, third, it may suffer elastic scattering. We shall find that the first two dominate the picture as far as the over-all energy loss is concerned, although the third exercises an important influence in determining the actual path of the electron.

Consider first, then, the problem of how a moving electron interacts with a system consisting of atoms which do, or can, oscillate. Here, in much of what I am going to say, we have very little information and have, for the most part, to be guided by general considerations.

The theory for the "inelastic" energy transfer from a slow electron to a molecule -- an isolated molecule, now, and therefore one in the gaseous phase -- is available only for two special cases, neither of them properly applicable to our problem. In the first instance there is a paper published many years ago by Massey (2) treating the impact of an electron with a homopolar diatomic molecule, that is, a symmetrical one of the type H_2 or N_2. In the second, there is a paper by Wu (3) treating the interaction of a slow electron with a molecule bearing a dipole moment which is comparatively small. This is also interesting but not quite relevant because we have to concern ourselves, in considering water or an aqueous medium or a biological system, with molecules, the dipole moment of which is great (in atomic units, e.g., comparable to unity). Therefore, from these studies we can learn comparatively little except that the probability of transfer of oscillational quanta to the molecule in impact is appreciable under certain circumstances; as a matter of fact, the excitation curve in the two cases that I have named looks a good deal like most other types of excitation curve. It starts at a threshold, rises to a maximum, and then declines with increasing energy.

There is one case, other than the interaction of electrons with isolated molecules, that is known quite well. That is the loss of energy of a moving electron to lattice oscillations in penetrating a polar solid such as an ionic crystal. This case is not entirely dissimilar to those that I mentioned previously and is, indeed, in some respects closer to the case of an electron in water than either of them. For this problem, which is of the greatest importance in many aspects of the physics of solids, there is a quite adequate theory developed by Fröhlich (4).

ONSAGER: There is some recent work on dielectric breakdown.

PLATZMAN: We shall not be concerned with dielectric breakdown. The over-all picture of dielectric breakdown involves a great deal more than what we require here and it is still not a little obscure. Fortunately, it is one of the things we don't have to worry about.

If we consider our single electron to have kinetic energy W, then Fröhlich has derived an expression for the rate of energy loss, - dW/dt. When I refer to the rate of energy loss I mean, literally, *rate* of energy loss and not -dW/dx. This theory applies immediately, of course, to polar solids, but has to be modified drastically if one wishes to apply it to the case of an electron penetrating water. This I have tried to do in a crude way. I think the result is probably correct to within an order of magnitude, and it gives the following:

$$(-dW/dt)_{vib} \sim 10^{13} \quad \text{ev/sec}$$

at an energy of several ev. For lower energies -dW/dt increases as 1/v. This will be the contribution to the rate of energy loss of the electron arising from the loss of oscillational quanta to the medium. This means excitation of molecular vibrations. It is evaluated numerically for the case of liquid water.

ONSAGER: Could that be rather closely correlated with the infrared absorption of water?

PLATZMAN: Yes.

ALLEN: Has this result something to do with the size of the permanent dipole moment?

PLATZMAN: Yes. I am, in effect, assuming that each molecular vibration corresponds to a certain component of the spectrum of lattice vibrations of a crystal.

ONSAGER: This order of magnitude involves the motions which can take up energy here, the motions of hydrogen atoms relative to the oxygens, and primarily the vibrations. I think the hydrogen atoms here could be very nearly free atoms.

PLATZMAN: A further point about this result is that it applies only down to a certain minimum velocity. When the electron's energy goes below that of the first oscillational level of the water molecule it cannot lose any more energy in this manner. The quantity dW/dt goes to zero. Indeed, it in fact becomes positive -- about 10^{11} ev/sec. That is to say, there will be a certain tendency for electrons to *acquire* energy from the oscillations. In somewhat different words, the electron can absorb as well as emit vibrational quanta; however if its energy drops below 0.2 ev, only absorption is possible.

KASHA: Are you referring to a single vibrational frequency? There are several.

PLATZMAN: There are three normal vibrations, but their frequencies are roughly the same. Actually one is at about 0.2 ev and the other two are at about 0.5 ev. When I say lower than this energy, I mean lower than the lowest of the three, i.e. 0.2 ev.

Let us now summarize what has been said. The rate at which a moving electron loses energy in exciting molecular vibrations is a function of the velocity, and is of order of magnitude 10^{13} ev/sec in the energy range between several ev and about 0.2 ev. Below that value (dW/dt) is actually positive, but is small enough to be unimportant.

ALLEN: How does this compare with what you get for the homopolar case?

PLATZMAN: It is considerably greater. The excitation of molecular vibration in the homopolar case is quite small. I might mention that, as far as experimental information on this very important question is concerned, there is very little. There were good experiments done by some students of Franck many years ago on the homopolar case. For example, the probability that an electron, passing in the vicinity of H_2, excites its vibration was found to be about 1 per cent. This shows that one must be careful about associating this process with the existence of a permanent electric dipole moment. No experimental work of this type has been done which can be taken as an indication of the energy loss to such a dipolar molecule as water.

MAGEE: Why do you discount the work of Bailey and Duncanson (5) with H_2O?

PLATZMAN: I haven't discounted it yet. I am going to discount it in a few moments.

Controlled impact experiments on the loss of energy of very slow electrons to important dipolar molecules, then, have not yet been undertaken. The only experimental work on dipolar gases that is available is that from drift experiments -- for example, measurement of the mobility of electrons as an electron swarm having some kind of thermal or pseudo-thermal velocity distribution passes through the gas. This is the case, for example, with the work of Bailey and Duncanson on H_2O that Dr. Magee mentioned, and that he and I have debated. I have lately tried again to find out how one can interpret the electron-swarm experiments and arrive at any information of significance to the problem we are discussing. My conclusion is that one cannot, at least not easily. These experiments, in my opinion, are not so interpretable at the present time -- at least not by me. In any case, they refer to the vapor and not to the condensed phase. And this makes a great deal of difference, as we shall now see.

Now I shall proceed to the second type of interaction, the interaction of the moving charge with the dipole moments, considering the molecules as rigid dipoles. This is an interesting problem which, incidentally, has never been treated before. I was very fortunate to have the collaboration of Professor H. Fröhlich, who was recently a visiting professor at Purdue, for this work. Together we worked out a simple theory for the rate at which a moving electron loses energy through rotation of the dipoles (6). This is related to rotational excitation in the gaseous phase, but is, of course, a quite distinct process. The principle of the method which we used, in physical terms, is to replace the moving electric field of the electron by an equivalent radiation field consisting of virtual photons; once that is done it is comparatively east to calculate the energy loss because one knows the absorption due to the rotating dipoles. This is just the dielectric absorption and is well known, for example, in the case of water,

The result is:

$$\left(-\frac{dW}{dt}\right)_{dip} \sim \frac{e^2(\epsilon_s - \epsilon_{ir})}{\tau d n^4}$$

Here, e is the electronic charge, $(\epsilon_s - \epsilon_{ir})$ is the difference between the static dielectric constant, which for water is about 80, and the high frequency or "infrared" dielectric constant. The latter is the effective dielectric constant in the infrared spectral region, and for water has a value which is comparatively large -- about 5. Further, n is the optical refractive index, d is the molecular diameter, and τ the relaxation time.

One striking thing about this result is that it is almost independent of velocity, and of about the same order of magnitude as the oscillational loss, for our electrons. If the electrons have energy below about 0.2 ev, it is, of course, greater.

KAMEN: How does it happen that velocity does not come in? I would think that both kinds of excitation would be dependent on velocity.

PLATZMAN: They are, in a sense. The formula is usually given as (-dW/dx), and this is 1/v times (-dW/dt).

Once the electron gets below an energy of about $\frac{1}{2}$ev, d has to be replaced by the de Broglie wavelength, and this puts a "v" in the numerator which starts to decrease the rate of energy loss below that energy. This effect is not important.

We have, finally, the elastic scattering, and this I know virtually nothing about. I would only like to take the opportunity to point out that I don't think many other people know much about it either since this is not the elastic scattering by single water molecules; once we get down in the low energy region the wavelength is big enough so that the electron always interacts with several water molecules at once. In complete ignorance, one can make the usual assumption that the scattering is isotropic with a cross section of the order of the molecular cross section.

KAMEN: Isn't that pretty large, comparing it to the energy loss?

PLATZMAN: Elastic scattering gives practically no energy loss. It very definitely dominates the picture for the actual path of the electron; however, you can find, in the new book by Massey and Burhop (7), which is a great boon to fundamental work in radiobiology, information on the elastic scattering of electrons by water molecules in the gas; it is relevant but not very relevant.

ONSAGER: That might affect the distance at which the electron finally comes to a relative rest.

PLATZMAN: It must affect it very much.

ONSAGER: Could you give us an idea of what the order of magnitude is?

PLATZMAN: That is just what I was going to do. So far I have talked about the individual mechanisms, but now I am going to try to consider them together and arrive at some estimates for the electron path. It is very easy to calculate how long it takes an electron to go from 5 or 10 ev to thermal energy, and this turns out to be very roughly 10^{-13} second. It is very important to note that this time is considerably greater than the reciprocal of the infrared absorption frequencies.

KAMEN: This is water vapor?

PLATZMAN: This is for liquid water, and that time, of course, involves the density.

ALLEN: When you go to 50 electron volts do you have any idea of how much of the stopping power is contributed by this?

PLATZMAN: About 0.1%.

ALLEN: That is, at 50 electron volts it is about as important or unimportant as at one million?

PLATZMAN: About. Within a factor of 10.

To return to the argument: The average time required for an electron to be moderated from the lowest electronic excitation potential down to thermal energy is about 10^{-13} second. This time is much longer than the reciprocal of the infrared frequencies -- i.e., the vibration periods of the molecule. Hence, in the period during which the electron is slowing down, there is ample time for the infrared polarization of the dielectric to develop, which means that once it is thermalized, the electron is surrounded by polarized medium to the extent given by a dielectric constant of five.[1] That is important.

POLLARD: What is the positive ion doing all this time?

PLATZMAN: I am glad you mentioned that. I have ignored the influence of the field of the positive ion on the electron. It is, of course, pulling the electron back. However, I have not considered this effect in detail yet. I do not believe, at the present time, that it will be of paramount importance. This is where Dr. Magee and I depart very much from each other in our interpretations. He will have ample opportunity today and tomorrow to bring this out.

POLLARD: Doesn't Coulomb's law hold?

PLATZMAN: Coulomb's law certainly holds, but I do not believe that the

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[1] At the time of the meeting, I had not taken into account the effects of the "resonance absorption" part of the dielectric absorption. Further work has indicated that this is highly important in the case of liquid water. It seems likely, however, that it will affect the conclusions I have drawn only quantitatively, and not qualitatively. R. L. P.

field is strong enough to bring the electron back (as Dr. Magee claims). I might point out that one must beware of identifying "Coulomb's law" with a simple, static $1/r^2$ force between the positive ion and electron. Actually, all of the polarization charges participate; moreover, the problem is a complex dynamical one.

ALLEN: I don't quite follow your statement about the dielectric constant. Relaxation time may be of the order of 10^{-13}, but the electron may pass through many molecules in that time. The time it takes to go through one molecule will be pretty much shorter.

PLATZMAN: Most of the polarization comes from greater distances.

ONSAGER: The charge is in the medium, moving in the direction of the electron. The electron is moving so the effect of the motion of the charge in the medium is a sort of compromise between the position where the electron is and the position where the electron was. The result is that there is on the average a drag felt on the electron. There is a time lag in the adjustment of the molecules here.

PLATZMAN: Thus far, we have found the total time for the energy to be dissipated. The total path length is much harder to calculate. That is, to say the actual total path length is easy to calculate, but the path is tortuous. Here all we can do is assume perfectly random scattering at every encounter with a water molecule. One finds the following figures, which are highly tentative: The actual distance measured along the track is of the order of 10^{-5} cm. and, therefore, the separation of the final and initial points is the geometrical mean of this and the molecular diameter, or about 50 Å. I am inclined to think that this is a minimum estimate. In any event one can at best expect that it is correct only to order of magnitude.

MAGEE: The path is measured from the positive ion?

PLATZMAN: Yes.

ALLEN: That is the root mean squared distance?

PLATZMAN: Yes.

ONSAGER: There may be some subtle effects which would tend to hold the electron a little closer to the origin.

PLATZMAN: Yes. For instance, the charge of the positive ion would tend to do so.

BURTON: So the electron would not be randomly scattered. It scatters inward all the time, so that one would say your estimate of the positive ion - electron separation is definitely too great.

PLATZMAN: No. I don't think that the field of the positive ion will have much influence on the electron until, perhaps, it is slowed down to near thermal energy. The internal field of a water molecule is, after all, very great.

MAGEE: What is the infrared value of the dielectric constant?

PLATZMAN: About five.

MAGEE: I believe that even so the coulombic energy at 50 Å is more than 0.04 ev at that point, isn't it?

PLATZMAN: Yes. But I believe that one must be wary of drawing any conclusions from that simple fact.

The preceding discussion has all applied to liquid water at room temperature. With ice, for instance, τ is very much greater and the rate of energy loss by dipolar relaxation becomes so small as to be entirely negligible. Once they get below 0.2 ev, therefore, the electrons just move around for a long time; perhaps here is where the charge of the positive ions would dominate the picture.

KAMEN: May I bring up a point? What happens when you substitute ammonia instead of water?

PLATZMAN: The figures should be of about the same order of magnitude, except for one qualification: I don't believe that anybody knows the value of ϵ_{ir} for ammonia.

KAMEN: I was looking for some explanation of why ammonia is so different from water as far as the length of time the electron exists in the free stage is concerned.

PLATZMAN: That I will come to later. I believe that this is easy to understand, but it does not concern what we have thus far discussed.

This ends the consideration of electron moderation. We now have electrons of thermal energy, and there arises the question of what happens to them. For years we have been saying that the reaction that takes place is

$$e^- + H_2O \longrightarrow H + OH^-.$$

This is the basis for the interpretation of radiation effects in water given by Dr. Burton and Dr. Allen and by so many others.

BURTON: The ideas in reference are properly to be attributed to Franck in the first place. Dr. Allen and I were both involved in the development of the theory when it was still entirely secret; the most interesting later features were entirely Dr. Allen's contribution.

PLATZMAN: I should now like to examine the physical mechanism of this reaction in some detail. First let us consider the energetics. Here we might be interested in either of two distinct reactions:

$$e^- + H_2O_{liq} \longrightarrow H_{aq} + OH^-_{aq} \qquad (A)$$

and

$$e^- + H_2O_g \longrightarrow H_g + OH^-_g\ , \qquad (B)$$

which refer to the liquid and gaseous phases, respectively. In both cases the electron (e^-) is to be though of, insofar as the energetics are concerned, as one which is not interacting with the medium. Then the heats absorbed in the two reactions, ΔH_1 and ΔH_2 respectively, differ chiefly by the "heat of solution", or "hydration energy," of the OH^- ion.

Although it would be difficult to think of simpler reactions in radiation chemistry than (A) and (B), it has not heretofore been possible to arrive at entirely satisfactory values for ΔH_1 and ΔH_2. This is to be ascribed to the fact that one does not have adequate information concerning the OH^- ion -- e.g., its heat of solution in water and the electron affinity of OH. The reactions were considered carefully by Dr. Magee and Dr. Burton (8), who for the first time, to my knowledge, pointed out (reference (8), page 532) that reaction (B) is endothermal, and that (A) therefore proceeds only by utilizing the hydration energy of the OH^- ion. This important conclusion apparently did not make the impression that it warrented.

I should like at this point simply to mention a new way of attaining a value for ΔH_1. On the basis of a recent theory (9) of the absorption spectra of ions in electrolytic solution, it is possible to deduce ΔH_1 from the position of the maximum of the characteristic absorption spectrum of the OH^- ion in water; this deduction is independent of any assumptions regarding the electron affinity of the OH radical or the hydration energy of the OH^- ion, and is contingent only on the applicability of the aforementioned theory. The result is: $\Delta H_1 = -1.6 \pm 0.2$ ev. For the reason already mentioned, it is not possible satisfactorily to translate this to a value for ΔH_2, but a crude estimate places the latter at, very roughly, $+2$ ev. These calculations entirely confirm the previously mentioned assertions of Dr. Magee and Dr. Burton.

I now come to a further point which is, I believe, entirely new: reaction (A), just because (B) is endothermal, runs into difficulty with the Franck-Condon principle, and is probably impossible. This is immediately apparent from an examination of the nature of reaction (B), which is an elementary process of the type called "dissociative attachment". For a simple molecule, a process of this type is essentially completed in (i.e., cannot be reversed after) a time of the order of magnitude of 10^{-13} second. But if the energy of hydration is to be utilized to satisfy the energy requirement, a time of 10^{-11} second, the dielectric relaxation time, is needed. In simple terms, this disparity in time means that instead of being captured by and dissociating the water molecule, the electron simply moves on. I therefore suggest that we have been mistaken in the past in presuming that reaction (A) is important in the radiation chemistry of water and aqueous systems, if the electron is "free" -- or, more accurately, is only weakly interacting with the medium, i.e., interacts only by the electronic polarization. Rather, the thermal electrons have a relatively long lifetime of at least the relaxation time (10^{-11} second), diffuse a comparatively great distance (of the order of microns), and are ultimately "captured" or "trapped" by the medium as a result of the dipolar relaxation. It seems likely that only after all of this has occurred can the dissociative attachment (A) take place. Perhaps the most important consequence of such behavior would be the existence of track effects for the OH radicals but not for the H atoms.

I should say that this presentation has been necessarily oversimplified in a number of respects. For example, it is conceivable that a free electron is attached in a process, to be thought of as one involving a very large polyatomic molecule, in which the energy defect is provided by a slight orientation of the water molecules about the OH^- ion. Such slight twisting is possible in the case of water; it can occur much more quickly than the true dipolar relaxation, and is responsible for the high value of the infrared dielectric constant. It seems likely, however, that such a process, even though energetically possible, has a very low probability.

FANO: The electron is not solvated?

PLATZMAN: The electron must be solvated first. The reaction will then proceed, but more time will have elapsed.

ONSAGER: It would require the dielectric relaxation time.

PLATZMAN: Yes, a minimum of that.

ONSAGER: It might be a little slower perhaps.

PLATZMAN: You see, the electron is moving.

ONSAGER: On the other hand, you have the mobility of the hydrogen ion, and that conforms about to the dielectric relaxation time anyway.

PLATZMAN: Well, it is probably of that order of magnitude. At least, it is much longer than the moderation time. It makes a delay in the chemical effect. A very pronounced delay.

BURTON: If this is inappropriate at this time just tell me. What about the process of the electron being captured by a hydrogen ion in the water? Have you thought about that?

PLATZMAN: No. Not yet. The studies which I have been describing are far from complete.

ONSAGER: As a matter of fact, this reaction goes even in ammonia. The reaction of the capture of electrons.

PLATZMAN: I was going to come to that in just a moment. I still have not suggested how the prior orientation of the dipoles will contribute the required energy. Ordinarily, if a charge is inserted into the dielectric, and the dipoles orient, the energy goes into heat: it is dispersed and lost.

First, however, I should like to take just a moment to explain to you how one can probably account for the properties of the "free" electrons in liquid ammonia[2]. This is a familiar system in inorganic chemistry. It is known that if alkali metals are dissolved in liquid ammonia, the solution develops an intense blue color and has a number of other striking properties. The interpretation is essentially this. Consider liquid water or ammonia. First of all, for the moment, ignore completely the possibility of chemical reaction. Take a charge and insert it at some position in the dielectric and see what happens. Obviously, the dipoles in the neighborhood will rotate. If we then remove the charge very quickly there will be left a region in which the electric potential has the shape of a potential well. It is easy to show that such an arrangement of dipoles will bind an electron in a number of quantized orbits. If the energy of the first excited state is calculated, the difference between it and the ground-state energy is that of the transition responsible for the blue color. This checks very well with experiment. In ammonia solvative capture is the only thing that can happen, because all possible chemical reactions of the electron absorb energy; therefore, the electrons are chemically stable. The difference between water and ammonia is simply that a chemical reaction of the electron, with negative ΔF, is possible in water. Solutions of these electrons in ammonia are therefore very stable if the ammonia is pure. Usually, however, it is found that they decompose over a period of weeks.

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[2] The discussion in this paragraph is based on an unpublished paper by the speaker. R. L.P.

BURTON: In other words, you are simply saying that the mechanism of reaction here in water can be to give a hydrogen atom, but in ammonia two solvated electrons have to combine to give H_2. A path must be provided for that to happen.

ONSAGER: That does not happen.

BURTON: No, I don't mean it happens in a single process, but a path has to be provided for it to happen.

ONSAGER: A catalyst has to be provided. You have to make not H but H_2, and you can keep the concentrated solution of sodium for weeks.

KAMEN: Why isn't the reaction (B) observed in electron bombardment? The required 3 volts could easily be provided.

PLATZMAN: I believe that it is, but the cross-section is very small.

KAMEN: Actually all that has been observed (in the vapor) is the H^- ions (10).

ALLEN: Do I understand you think that irradiated ammonia ought to turn blue if it is pure?

PLATZMAN: More than that. I think irradiated water does turn blue and we just don't see it.

ALLEN: The fact is that irradiated ammonia does not turn blue enough to see, whereas if you dissolve sodium in it there is no question about it.

PLATZMAN: It is a question of the recombination time.

ALLEN: The sodium is the thing that stabilizes it.

PLATZMAN: No. It is the absence of reactive positive ions. The point is that if you irradiate you have the reactive NH_3^+ ions.

ALLEN: In the sodium solution you have just as many positive ions.

PLATZMAN: But they are of a quite different nature.

MAGEE: That is an equilibrium process, too, and when the sodium gets hydrated they have essentially no field around them.

ONSAGER: Very little field.

MAGEE: This is a steady-state condition.

PLATZMAN: It is important, in discussions like the present one, not to lose sight of the very great difference between an "electrolytic" ion and one freshly formed -- e.g., by ionizing radiation. This difference may be brought out by a consideration of the recombination energy of H^+ and OH^- ions. In the gaseous phase, this recombination would evolve about 370 kilocal/mole. In aqueous solution, however, the heat of neutralization is only about 14 kilocal/mole. What happens to most of the recombination energy? One way to visualize the answer to this question is to consider each electrolytic ion surrounded by its hydration shell, an "iceberg" of frozen water. When the electrolytic H^+ and OH^- ions encounter one another, most of the recombination energy goes to melt the icebergs.

ALLEN: What is the difference in ammonia?

MAGEE: The steady-state concentration of electrons and NH_3 positive ions, solvated or not, is just zero. You don't have ionization in ammonia.

ALLEN: We irradiated ammonia. In fact, the result has been published (11). There was no blue color. Nothing happened.

PLATZMAN: During irradiation?

ALLEN: Yes, during irradiation. If we had obtained color you would have seen a paper in the journal, but since we didn't get any color there was just a little note.

BURTON: An important question was asked and Dr. Onsager was answering it. Essentially it was this: What is the ion product constant in ammonia?

ONSAGER: I don't think anybody knows.

BURTON: Is it lower than that of water?

ONSAGER: Definitely. I think ammonia has been produced with a conductivity of about 0.01 that of water.

BURTON: Let us consider some relatively simple processes in pure ammonia. Ionization will give the reaction

$$NH_3 \rightsquigarrow NH_3^+ + e^-$$

The important question revolves around the fate of the electron. Does it recombine with the parent ion? Is it captured by another NH_3^+ ion? Or is it captured by the liquid to give a trapped electron. If the latter process makes a significant contribution, the solution should become blue. Absence of a blue color in Dr. Allen's experiments certainly shows that no significant steady-state concentration of solvated electrons was produced. However, the explanation of such absence is not clear from the data at hand. The important question remains whether color (and therefore electron solvation and electron movement away from the parent ion) would have been detected at higher radiation intensities.

PLATZMAN: Did you look at it <u>during</u> the irradiation?

ALLEN: It is a little hard to say. We had cathode rays going in. However, we had the electrodes set a little back, so that the region right between the electrodes was not actually in the path of the beam. There was no rise in conductivity that we could measure during the bombardment. So if these electrons had lasted long enough to diffuse a few millimeters we would have seen them. After the irradiation there was no blue color. We also did this with X rays at 50 r per second, and again there was no change in the conductivity.

PLATZMAN: There is another way to approach this. Make ammonia out of tritium, take a long tube of it, and see if it is blue.

ONSAGER: There is another experiment that is germane here. The sodium solutions in ammonia give pronounced photoelectric effects, extending to quite long wavelengths. You can kick electrons out into the vapor phase with a very modest amount of energy.

BURTON: The trapped electrons?

ONSAGER: Yes, and I think there are absorption spectra here in the infrared.

PLATZMAN: That is correct. The theory I mentioned agrees with this.

KASHA: Does it account for the broadness of the bands?

PLATZMAN: I don't yet know.

ONSAGER: As regards the picture itself, I think there is one point that is not brought out. You might have intended to bring it out and forgot about it. It is that the hole the electron makes for itself is pretty big. As regards the size of the hole, opinions have been varied. DeWall spent last year with us. I believe he looked into the question rather critically and he thought that 70 cubic centimeters per mole was about right at low concentrations. It is certainly at least 40. On the other hand, not nearly as big as suggested by Ogg many years ago, although Ogg does have credit for some perfectly good experiments (12).

PLATZMAN: Let us now proceed with the "life-history" of the secondary electron. Since the dissociative attachment is impossible for a free electron, it must wander around until it becomes hydrated. We can assume that in this state it is very similar in properties to the blue electrons of ammonia, because the dipolar and dielectric properties of water and ammonia are very similar. Now, if dissociative attachment to one of the water molecules about which the electron is spread occurs, there is made available the increase in energy with respect to the polarized dielectric corresponding to the electron "collapsing" about an OH radical. This provides the necessary 2 or 3 ev. In another sense, the electron moving in the field of the dipoles has a great deal of kinetic energy; when it is attached to the radical it does not have to have that and regains the entire potential energy at or near the bottom of the potential well. This is one of the major points that I should like to make this afternoon.

MAGEE: Have you essentially completed your picture? Could you summarize and give us a complete picture, especially of where these things happen?

PLATZMAN: Let me review it briefly. I will start back at the point where we found that the 10-volt electron takes about 10^{-13} second to be thermalized. In this time it goes about 10^3 Å, and, on the average, its actual final separation from the positive ion is about 50 Å, both of these being minimum estimates -- this, however, neglecting the factor of the electric field of the positive ion, which which would reduce them. Having attained thermal energy, the electron finds it impossible to carry out the chemical reaction which is written in all the articles on radiation chemistry, just because of the disparity between the time the actual reaction takes and the time which would be required for it to utilize the hydration energy which makes it possible. For this reason the electron becomes hydrated. One must, of course, be very cautious about using the word "hydrated" because it means so many different things to different people. I mean here that the electron polarizes the dielectric and is bound in a stable quantum state to it. Then, finally, the chemical reaction can proceed as I have suggested, and the OH^- ion and H atom are formed. In between there is the time for the hydration to take place, which must, as Dr. Onsager said, be a minimum of the relaxation time 10^{-11} second. It may be greater; I have been trying to calculate this time by applying the theory suggested by Landau for the polarization of a crystal which turned out to be wrong for the crystal case but, I think, might apply here. I don't have any results to report on this, as yet. It does not concern the main picture because we are certain that the time cannot be shorter. The energy of the hydrated electrons, that is, the total energy of solution, by analogy to the case of ammonia, turns out to be about 2 electron volts, and the mobility of the "trapped" electron turns out to correspond to an effective electron mass of about 1/5 of an ionic mass.

The second important "delay" is that required for the hydrated electron to dissociate into H^+ OH^-. It is amusing to note that this process bears close analogy to orbital capture of an electron by a nucleus. There, too, the electron collapses and produces a permanent change. I have not yet been able to calculate the time required by this process; a preliminary and rough estimate gave 10^{-9} second. On this time hinges the possibility of observability of the transient hydrated state of the secondary electrons. If they should be fairly stable in the hydrated state, they might conceivably be observable. If the time is very short they probably never can be, except indirectly through their influence on the chemical kinetics.

BURTON: In terms of your own restriction I think the statement must be modified. You said this is physically pure water. After all, there are competing processes in real water.

PLATZMAN: All of them would tend to shorten the total time.

To get an idea as to the observability by optical means, suppose that we took a column of pure tritium water about 10 centimeters long and looked for the blue color. What would the lifetime for attachment have to be in order to observe it? It turns out that it would have to be at least 10^{-5} second, which is highly unlikely.

LINSCHITZ: I don't quite see the mechanism by which you use the solvation energy of the electron to help process (A) go. How do you couple the solvation energy around the electron to any other process that would help you hydrate the OH?

PLATZMAN: The water molecule to which attachment takes place is supposed to be inside the "orbit" of the electron.

LINSCHITZ: It has to be inside the same hole.

PLATZMAN: There are several water molecules inside the orbit. Attachment to one outside would not take place.

LINSCHITZ: This electron is by itself and if you use it essentially to make a hole in the solvent----

PLATZMAN: There is no actual hole there. I don't like that word. It is often confused with the "potential well".

ALLEN: There is a real vacancy there. When these things orient they expand somewhat.

PLATZMAN: They push apart. That is correct. The density becomes smaller. This is known not only in the figure that Professor Onsager cited; it is also known from the crystal, when electrons are trapped. But this does not mean that a "hole" is present.

LINSCHITZ: If you hydrate the OH which is going to be formed on the side of this structure, isn't that the problem?

PLATZMAN: No, because there is no vacuum inside the orbit. There may even be one water molecule preferentially close to the center.

LINSCHITZ: So you are really hydrating over quite a volume?

PLATZMAN: Of course. The radius is quite large.

ONSAGER: Shall I talk about a competing process, because I think it can settle the recombination question? Ionic recombination processes cannot go any faster than the ions can find each other, and there is an old theory, fifty years old, for recombination of this positive and negative ion. It depends just on mobility and the dielectric constant.

PLATZMAN: What is the relaxation time?

ONSAGER: You get about the right result if you use the formula for the Maxwell relaxation time, and feed into it the sum of the concentrations of the recombining ions, and the arithmetic mean of their mobilities.

PLATZMAN: What order of magnitude?

ONSAGER: At the conductivity of water, it would be about 10^{-5} second.

BURTON: Does your statement apply to solvated electrons plus solvated hydrogen ions?

ONSAGER: It does.

PLATZMAN: It doesn't matter.

BURTON: I would like you to consider the unsolvated electron plus the solvated hydrogen ion.

ONSAGER: This is the minimum time it takes for two ions solvated or unsolvated. It does not matter. They have certain drift speeds, and it turns out that the electrostatic attraction is more important than just a purely random motion.

PLATZMAN: You still consider that to be correct in order of magnitude?

ONSAGER: It is still a minimum. There might be other steps and the process might be slower. But, of course, the ions cannot react before they get together.

BOAG: You are assuming a random distribution of the ions whereas they are actually produced in high local concentrations.

ONSAGER: The question is whether the electrons will be combined with the hydrogen ions that happen to be present in the water to begin with.

ALLEN: What are the concentrations here? I don't quite understand your relaxation time.

ONSAGER: If the concentration of H_3O^+ is what it happens to be in pure water, it is 10^{-7}.

ALLEN: Two ions and they are each 10^{-7} molar. Then the combination time is about 10^{-4} second or something like that.

ONSAGER: Yes.

ALLEN: This is just from electric attraction alone. This does not take into account thermal motion.

ONSAGER: Thermal motion did not make any difference. That is a pretty result of Langevin's theory (13).

PLATZMAN: What I have suggested, then, is that after the electrons are thermalized by the processes mentioned, there occur two possibly rather time-consuming steps, in succession. First, the hydration, or "trapping" of the electron, and second, the attachment of the hydrated electron to the OH radical. Each of them probably consumes a minimum of 10^{-11} second, the latter probably a good deal longer. "Trapping" of the electron might suggest that the distances from the positive ions reached by the ejected electrons are not, after all, very great. This is not true, however, because of the great mobility of the trapped electrons.

A further and final point concerns the observability of these trapped electrons. If I am correct, the trapped electrons will play a decisive role in constructing the chemical kinetics. It becomes very interesting to see whether these speculations can be substantiated or contradicted by experiments. However, unless there is something that we don't understand to prevent the attachment from proceeding once the electron is trapped, I doubt whether the color will ever be directly observable. There is still the possibility of measuring the conductivity of pure water during irradiation. I do not know about the feasibility of such an experiment. I found in the literature some alleged discoveries of augmentation of conductivity, but they are highly suspect.

ALLEN: The blue color would be a more sensitive test than the change of conductivity.

PLATZMAN: No. I don't think so.

ALLEN: Remember that the water has much conductivity to begin with.

PLATZMAN: Yes, that is correct. One would probably have to measure the frequency-dependent conductivity.

This is all that I wanted to say. I greatly regret the incomplete and tentative nature of some of these considerations. But, having to open the discussion at hand, I could not do otherwise than tell you of this new work. Let me return to my original remarks, which were that it is far from unlikely that the over-all picture I have given you will be found to be incorrect, at least in part. But still I feel reasonably confident that some of the scenery which we have been contemplating is authentic.

BURTON: Dr. Platzman, you say the hydrogen atom is formed substantially away from the region where the positive water ions appear?

PLATZMAN: Yes.

BURTON: On your picture would you expect any difference between the effects of alpha particles and slow electrons?

PLATZMAN: Yes.

ONSAGER: It occurs to me that it might be possible that dissociative capture goes a little faster in some way, because these two steps of making a hole for the electron and then attachment of the electron might be telescoped.

PLATZMAN: Yes.

ONSAGER: That the electron might attach directly, so that one hydrogen atom does not have to make a hole. After all, what makes the hydration is simply that the charge is here which gives rise to the orientation of dipole moments.

PLATZMAN: But you cannot telescope it too much. The dissociation requires approximately one vibrational period, and, therefore, about two electron volts of energy must be acquired during the 10^{-13} second.

MAGEE: I don't think there is a cross section known for dissociative capture in the gas that is greater than maybe 10^{-18} cm^2. They just aren't any bigger than that and most of them are even smaller.

ALLEN: What about Bradbury's experiments (14) on water vapor?

MAGEE: He didn't measure anything greater than that.

ALLEN: That is because his instruments gave out. It went up too high for him to measure.

ONSAGER: Now let's translate that cross section into time. In the liquid, a cross section of 10^{-18} cm^2 corresponds, for a thermal electron, to a time of 10^{-12} second.

PLATZMAN: If the electron is hydrated, its thermal velocity would be somewhat smaller.

ONSAGER: Well, I guess with this effect we cannot expect much to happen then until the electron has been pinned down to one neighborhood. So it should be of the same order as the dielectric relaxation time after the electron has started orienting the molecules around it, or in moving about has found a place in which a water molecule happened to be pointing the right way. It wouldn't, I think, find many places. That is a question of potential fluctuations in water. It might actually be that the electron starts out by finding a place where, thanks to the accidental orientation of the water molecule, the potential is a little high, where the potential might be 0.3 or 0.4 of a volt plus, and then the electron lands there and stays in the neighborhood, and the water molecules around gradually fall into place and the potential drops. We might have to visualize the process that way.

PLATZMAN: Essentially, I believe that it is proper to say that the modes of energy loss of the swiftly-moving electrons are essentially correct as I have given them. The other questions to which the answers are uncertain are: the time required for the capture of the electrons by the dipoles; secondly, the time required for dissociation after it is captured; and, third, consideration of the many things that I have neglected, namely, the electrostatic field, time variations, impurities, etc.

BURTON: Dr. Platzman, perhaps I should not say this but you still have a time in there of the order of 10^{-10} second and you have a figure for the thermalized electron-parent ion separation of 10 to 50 Å. Isn't another very important competing process, that really can occur very well, the recombination with the parent H_2O^+ ion?

PLATZMAN: No, I don't think so.

ONSAGER: That can be analyzed. I think it might occur. It isn't too probable. The chance of escape is simply the Boltzmann factor for the electron at whatever distance it slows down to thermal velocities.

LINSCHITZ: We have tried actually to measure the lifetime of the presumed blue color in irradiated water, using pulsed X rays. The radiation was passed transversely through a water cell 1 cm in diameter and 15 cm long, while we looked down the tube with a monochromator and photocell. The X rays were taken from a Westinghouse "Micronex" outfit, at about 150 kv, with a pulse duration of about one microsecond. The dose-rate was something like 10^5 r per second and with an oscilloscope we could measure the absorption up to within 10^{-5} seconds of the pulse. In no region of the visible spectrum could we see any absorption that might correspond to electrons in water.

PLATZMAN: Of course, the absorption would be continous throughout the visible region, and would disappear in a time much shorter than 10^{-5} second.

LINSCHITZ: It might be that again the total intensity was not quite enough. I think we were just on the ragged edge.

PLATZMAN: Tritium water provides another possibility for finding this absorption.

POLLARD: I should like to speak before everybody else does. This is a group which we might say is dedicated to the subject of water. I should like to point out that your remarks are really a little broader in their implication. I should also like to point out that a whole lot of biology does not involve water. There is very little water inside a virus. The method of inactivation of the virus by water-borne agents is clearly different from that which is observed in the absence of water, or where water is kept to a minimum, and follows the line which is more normally accepted biologically. There is every reason to believe that there is a side of radiobiology which is not concerned with water at all but which is concerned with radiation mechanisms involving protein and nucleic acid, two quite interesting substances. What about your remarks? Suppose you did not consider this as something with a molecular weight of 18? What would happen if you considered this in a micro-crystal or a micro-molecule of protein or of nucleic acid? To what extent would several of the factors you discussed matter?

For instance, let's take the question of the force between the positive ion and the electron. Has the infrared dielectric constant been taken as 5.5 or is it less?

PLATZMAN: We know this only for relatively few substances. The value for H_2O, namely about 5, is extraordinarily great.

POLLARD: Yes, and it is likely to be considerably less. In that case, the tendency in the solid would be toward recombination.

That brings me to a further statement and that is the electron, while it may stay in the neighborhood in which it is formed, does not end up in water. Are there any plausible things you can think of connected with the polypeptide chain or with any of the amino acids or of the bases that are present in nucleic acid -- do any of these things come to mind as suitable places where electrons might go and sit down? Is there anything in the nucleic acid or the protein which is likely to take the electron before it gets back to the positive ion?

ONSAGER: Any carbonyl group.

POLLARD: And there are loads of those.

ONSAGER: As a matter of fact, an electron in ammonia will attach itself to acetone.

POLLARD: In other words, the polypeptide chain is the likely place where radiation action in the solid protein is likely to occur. How about nucleic acid?

ONSAGER: How about purine?

PLATZMAN: Do you suggest that the electron affinity of CO is greater than the energy of binding of the CO group to the rest of the molecule?

ONSAGER: There is a double bond in CO.

PLATZMAN: That is quite strong, isn't it -- the bond binding the CO to the rest of the system?

ONSAGER: All the electron has to do is to take up one state there and make it a three electron bond instead of the double bond.

BURTON: Is this a dissociative capture or mere capture here?

ONSAGER: This is capture which is not dissociative.

PLATZMAN: Not mere capture. Capture is very unlikely. So you should not use the word "mere".

BURTON: All right. I'll substitute "simple". Let's say that there are two possible processes. One is a capture process without dissociation and the other is a capture process with dissociation. If the capture process occurs with dissociation then this is an important thing. But if it occurs without dissociation, then what we are primarily concerned with eventually is how does the process of neutralization occur, and we may really say that what we are concerned with is how does the captured electron migrate toward the positive ion in these cases.

POLLARD: And does it do anything permanent on its way?

ONSAGER: If later water gets there --

BURTON: Let's stick to the dry case.

KAMEN: What do you mean by dry? Nothing is dry except the virus.

POLLARD: Protein.

KAMEN: Protein isn't dry. It still has water in it.

FANO: How much water is in protein?

POLLARD: As far as I am concerned, we need to talk about whether there is a place where the electron is admittedly more likely to be trapped in the immediate locale. Is there a place in the polypeptide chain where on its way back to the positive ion it can do positive damage? Is so, where is the likely place and let's think about that as a very important radiobiological process?

KAMEN: What is the ionization and what is the source of the electron?

POLLARD: Well, it has been kicked out of the atom.

KAMEN: What atom?

POLLARD: The carbon, hydrogen, nitrogen, phosphorus, or sulfur.

KAMEN: The best thing I can do is to take an amino acid like alanine and ask what happens.

KASHA: The electron would come off the oxygen probably, and form a free radical which would then dismute and give off CO_2 and then the electron meanwhile --

BURTON: Why do you form a free radical when you take an electron off something? Why does it immediately decompose?

KASHA: A charged radical is formed.

BURTON: Why do you have to produce it? What you produce initially is an ion.

ALLEN: It has an odd number of electrons.

BURTON: The electron moves some place and you leave an ion behind. It does not necessarily follow that the ion is chemically unstable. The ion might be stable.

ONSAGER: That is uncertain.

KASHA: This electron is not a bonding electron so that it would probably be stable. Wouldn't the two electrons be the non-bonding electrons of the oxygen?

BURTON: There is no requirement that it be any particular electron. You can get any electron out.

KAMEN: I think when you have a rearrangement of the electrons you are bound to break something.

LINSCHITZ: It is a known practice to make radical ions in various rigid solvents by photo-ionization. They may be quite stable if you can avoid back reaction with the ejected electron (Lewis and Lipkin (15)). We are going to talk at some length about that process in the fourth session.

KAMEN: The only things that are pertinent here are the data by those who have done the work. I imagine Dale has irradiated solid alanine and solid amino acid, has he not?

POLLARD: I haven't heard if he has.

BUTTS: There is such a study going on at Reed College.

POLLARD: We have radiated solid enzymes. There is no question in my mind that dry material is completely different from wet and this I base largely on the thermal inactivation of dry material. If you take a dry enzyme -- or a dry virus -- they follow the ordinary reaction kinetics when you inactivate them by heat. You get the ordinary monomolecular reaction, but the constants of the process are totally different; apparently the entropy of activation is low. One rather large source of entropy, breaking off water, is now no longer freely available, and this seems to be universal. It is not specific in any way. It applies to anything dry. You can just categorically say that of dry material the entropy of activation lies between 20 and minus 20 entropy units. I feel that you have in this, admittedly in a somewhat indirect way, evidence that you have a different material. There is an additional feature. If you have a small molecule the vapor pressure at the surface of the small molecule is about 7 per cent higher on account of the radius of curvature, just simply because of the surface; therefore, even if you put a small molecule which is wet into practically saturated air, it will tend to dry as regards that kind of vapor. So the only sort of vapor you can conceive of as being present in any material which is a high vacuum is presumably material vapor which is not vapor at all but which is bound, and if it is bound, I should like to ask the question is water of crystallization dry or wet? Is it bound by its hydrogen bond? That is the question. What I was thinking about was this Franck mechanism that you were beating around two years ago.

BURTON: A moment ago somebody asked whether any of these dry amino acids had been studied. Dr. Butts interjected the statement that some work has been going on at Reed College. I think we ought to hear about that.

BUTTS: I can tell you very generally what they have been getting. They have irradiated a number of amino acids. Cystine and tyrosine were two that gave very definite breakdown products, and, as I recall, serine was identified. They irradiated a great many other substances, but those are the two that stick in my mind particularly. It has been quite a while since I saw the report, but they reported these were in the dry state.

KAMEN: It is hard for me to see how you get serine from cystine.

BUTTS: I believe alanine was also reported.

GARRISON: Didn't they observe decarboxylation with that?

BUTTS: I don't recall.

GARRISON: It is my impression they did get decarboxylation.

ALLEN: Did they find that in the presence of air?

BUTTS: I don't know.

KAMEN: Did these people in this research find something significant in the fact that cystine is the most sensitive, or one of the most reactive, to radiation under whatever conditions they had?

BUTTS: Cystine is the one they found was the most sensitive to radiation.

BURTON: I don't know whether this is pertinent and maybe Dr. Onsager can tell us. Would cystine be a case where you could easily get dissociative capture? That is, would H come off very easily?

ONSAGER: I don't know much about it.

BURTON: The strength of the carbon-sulfur bond is rather low, isn't it? The HS would have a pretty good electron affinity.

ONSAGER: That might well happen. Others here would know at least as much about it.

MAZIA: I know that you cannot preserve cystine in solution for very long. It oxidizes readily, especially if the system is contaminated with traces of iron..

BURTON: My guess is that the S-C bond there is weak and that you should have dissociative capture there rather readily as well as at the carboxyl link.

BUTTS: You would criticize their experiments because they were done in air? Is that right?

POLLARD: Yes, I would.

BURTON: If you had air there, you would be in an uncomfortable situation in that oxygen itself captures electrons and that would tend to confuse the whole issue.

ONSAGER: In connection with the previous discussion, it might be of some interest to radiate dry water. I mean ice.

PLATZMAN: I believe that has been done, and it would be interesting to hear about it.

HOCHANADEL: Ghormley and Stewart at the Oak Ridge National Laboratory have been studying the radiation chemistry of ice. The study thus far has been chiefly that of the gamma ray induced formation and disappearance of hydrogen peroxide as a function of total dose, temperature, concentration and the presence of dissolved gas. Hydrogen and hydrogen peroxide are produced at all temperatures from 0°C down to -269°C. The initial yield decreases continually from 0°C down to -200°C below which it is nearly constant down to -269°C. Reactions occur in ice which lead to disappearance of peroxide, and on long irradiation, steady state concentrations are obtained. The initial rate of disappearance of peroxide in hydrogen saturated ice containing peroxide, increased with temperature in the range from -175°C to -50°C with a seven-fold increase in rate occurring between 100°C and -50°C. On irradiating ice at -196°C there was evidence for existence of unstable species such as free radicals or trapped charges which could be released in the solid on warming to temperatures above -180°C. This was shown both by chemical and optical measurements.

ONSAGER: Do you find any connection there with the dielectric relaxation of the ice?

HOCHANADEL: Complete correlations with the dielectric properties of ice have not been made, although a close similarity was noted in the variation with temperature between the yield for peroxide disappearance in hydrogen saturated ice irradiated with gamma rays and the dielectric constant of ice for a frequency of 60 cycles per second.

ONSAGER: Did you compare your times with the time of dielectric relaxation of ice?

HOCHANADEL: No such correlation has been made.

PLATZMAN: I might venture to suggest that it might not enter at all just because the relaxation time is so great that relaxation never occurs.

ONSAGER: It is not so very great.

PLATZMAN: It depends on the temperature, but once you get down --

ONSAGER: At the freezing point it is a few micro-seconds.

PLATZMAN: It is about 10^{-5} second at the freezing point. At -170°C it is many years.

I would suggest that if you never have relaxation at all, the electron moves rather freely.

ONSAGER: I don't know about that because you might have something else.

ALLEN: Can you tell us how long it will take this electron to be released at -170? When you raise the temperature up to there, does it come out in a matter of minutes or does it take hours?

HOCHANADEL: It is a matter of minutes.

Ghormley and Stewart showed by chemical and optical measurements that unstable species such as free radicals or trapped charges are produced in ice at low temperatures by gamma rays, and that these species can be released in the solid at higher temperatures. Chemical measurements of hydrogen peroxide, hydrogen and oxygen were made after melting the irradiated ice; however, by a method of thermal cycling with intermittent irradiations, the temperature range in which reactions occurred in ice after irradiation (presumably due to release of these trapped free radicals or charges) was determined. For example, when a sample of ice containing dissolved hydrogen peroxide and hydrogen was subjected to two or more ten minute irradiations at -196°C and allowed to warm to -180°C or above between irradiations, the observed final concentration of hydrogen peroxide was less than that for an equivalent continuous irradiation at -196°C. The presence of unstable species in ice irradiated at -196°C was also indicated by a broad absorption band with a peak at 2800 Å which disappeared on heating over a similar temperature range.

KASHA: I might make a comment about what Dr. Linschitz has already mentioned; that there is a small field of photo-chemistry in which people have irradiated organic molecules in rigid glasses, using both electrons and light. The "photo-oxidized" rigid solutions have been found to be paramagnetic. The solvated electrons are stabilized in the rigid glass solution and they remain that way until the system has been melted, after which they become unsolvated in a matter of minutes or fractions of a second perhaps. That can be judged very quickly by observations of the color phenomena which accompanies the desolvation of the electrons. You see, this work goes back to the work which Lewis and Lipkin (15) did.

BURTON: With electrons?

KASHA: No, other people used electrons. Lewis and Lipkin used light.

BURTON: Who are the other people who used electrons?

KASHA: Goldstein (16), I believe. It is very old work.

BURTON: They irradiated dyes in glasses with electrons?

KASHA: They irradiated molecular cystals of , not dyes, but somewhat simpler molecules. All of these people have found that induced colors are destroyed upon warming, and it turned out that the induced color is spectroscopically identical with the ion which you would produce from the substance electrochemically. So that the identification of the positive ion which may be made was complete and the only missing point was the electron, that is, its condition in the rigid system.

ALLEN: Was the observed spectrum of positive ions?

KASHA: Both are found actually, but in general the spectrum one finds is that of the positive ion. This involves details which I think will be brought out tomorrow.

LINSCHITZ: After ionization, due to high-energy radiation, a positively charged radical ion might lose a proton in an ordinary acidbase type ionization. Whether or not the residual radical has a charge would have a bearing only on the rate of recombination of the radical with the solvated electron that has been knocked out. So that in this instance it is relevant to what you might call the lifetime of the solvated charge.

BURTON: This is a crystal system?

LINSCHITZ: The systems in which these processes have been studied so far are glasses. In general such solvents are polar and vacancies exist in which electrons can be trapped. Let's leave out the mechanism of trapping the electron. When you do trap the electron you are bound to leave a positive ion, and under such circumstances it will have a characteristic color as will the trapped electron.

KASHA: It is found that which solvent is used is rather crucial. In other words, if it is a hydroxylic solvent, then these photo-oxidations, as they are called, proceed readily, but if it is a purely hydro-carbon solvent -- both of these experiments are rigid glass solutions at very low temperatures -- the purely hydrocarbon solvent does not show this phenomenon. That is, it does not apparently provide a site for the electron, and frequently photo-oxidation does not take place.

ONSAGER: With carotenoids as solvents?

LINSCHITZ: Do you mean as the trapping agent?

ONSAGER: Yes. It would also be a good source, because I believe they should be more readily ionized.

KASHA: It has been tried with nitrogen compounds like diphenylamine. Diphenylamine in a hydrocarbon solvent does not lose its electron readily, while diphenyl amine in hydroxylic solvents does.

BURTON: Are you talking about glass?

KASHA: Yes, glass in hydrocarbon versus hydroxylic glass.

ALLEN: I should like to get back to the ice for one more question. This concerns the blue color of irradiated ice. Does the ice retain its blue color for a long time above -170°?

HOCHANADEL: I am not sure that we have noticed the blue color.

GARRISON: Didn't you notice it in the cellulose in the cotton that you used?

HOCHANADEL: Both cotton and kleenex irradiated with gamma rays in liquid nitrogen appeared pale blue in color. However, this color was later attributed to the presence of ozone produced by the radiation.

ALLEN: As I remember, we used to see the blue color in irradiated ice.

HOCHANADEL: We thought we saw blue color in ice. However, recently we have irradiated large pieces of clear ice at -196°C and observed no visible color.

ALLEN: I was never sure it was the ice that was giving us the blue color, rather than the container.

PATT: I should like to interject a remark about the dry virus, which, I believe is pertinent to Dr. Pollard's earlier comment. An Argonne group (Bachofer et al) (17) X irradiated dried bacteriophage at different temperatures in a vacuum. They found that the inactivation efficiency decreased slightly, though progressively, when the temperature fell from 37° to -196°C. The effect was of the order that might be anticipated from an interaction with free radicals. Some water is doubtless present in a dried preparation of this sort and may contribute to the over-all inactivation.

POLLARD: Adams has worked on that. I have done a lot of work on it, too, quite independent of his work, actually, and in addition several members of my group have irradiated catalase at different temperatures, both with deuterons, X rays and ultraviolet, and there is a temperature effect in all cases. In the case of viruses, the virus has a definite internal structure. I think for one thing it has a protein coat and it has inside it a nucleic acid, and probably also water, which may stay in this protected by the protein coat. But I think that the real factor that concerns temperature in that case is the differential sensitivity of the different constituents inside. If merely a simple assay is made on only one it is very misleading, because it has a latent period, and if you allow for that, which corresponds to damage and not to complete knocking out of the virus, you get a totally different conclusion from the case where you actually assay for virus regardless of latent period. So until all these factors are sorted out, it is very dangerous to draw conclusions because there is a rate constant that you think might fit water. I refuse to draw any conclusion myself, although we have done a vast number of experiments on T-1 phage. Because of this factor, this internal structure makes it doubtful what one can do. Only lately we have found that if you irradiate with alpha particles, which we have done, the cross section fits pretty well with everything but the protein coat.

PATT: Since we are also concerned with the effects in ice, I wonder whether the chemists would care to comment about the work of Bonet-Maury. I believe that he measured hydrogen peroxide formation after irradiation of ice with X and alpha rays. These results have been considered in the interpretation of temperature effects in certain biological systems.

HOCHANADEL: One reason for our initiating a study of the radiation chemistry of ice was the observation of Bonet-Maury that no hydrogen peroxide was produced in ice irradiated with X rays at temperatures below -116°C. In contrast to this, Ghormley and Allen had found considerable gas production by self radiation in tritium ice at -196°C. In the present work, Ghormley and Stewart find peroxide in ice irradiated with gamma rays at all temperatures from 4° K to 273° K.

ALLEN: If you freeze de-aerated water and obtain ice as pure as possible, and you irradiate it with gamma rays while it is very cold, and then you warm it up, you say you do find peroxide, whereas if you irradiate when it is not frozen you do not find peroxide?

HOCHANADEL: In a sample tube containing no gas space, a low steady state concentration of peroxide is produced by gamma rays in liquid water near 0°C; however, this concentration is somewhat smaller than the steady state concentration in ice near 0°C. Both the yield of peroxide production and the yield of back reaction are probably larger in the liquid than in the solid near 0°C, however, the steady state concentration is lower in the liquid.

PLATZMAN: Does the yield decrease as the temperature declines?

HOCHANADEL: The yield for peroxide formation decreases continually with temperature from zero down to liquid nitrogen temperature below which the yield is nearly constant down to liquid helium temperature.

ALLEN: Right near the melting point you still get a big yield of peroxide?

HOCHANADEL: That is right.

ALLEN: Even though just above the melting point you would not find it?

HOCHANADEL: Near the melting point the steady state concentration is lower in the liquid than in the solid.

BURTON: The rate at which you come up from the low temperature will have a great bearing upon the results that are observed because you observe your results only in liquid water.

HOCHANADEL: A study of the effect of rate of warming of the irradiated ice has not been made, although no appreciable effect is expected.

ZIRKLE: Is this work in report form anywhere?

HOCHANADEL: This work is published in Oak Ridge National Laboratory, Chemistry Division quarterly reports. Papers will be presented both at the Radiation Research Society meeting and at the Gordon Research Conference in June. A paper will also be submitted for publication in the open literature very soon.

POLLARD: There is a way by which you can use all cosmic ray data without changing the data to tell you the average of primary ionization. It does tell the number of places where events will happen. This works out from data purely taken from electrons, which is rather unfortunate, to be 110 volts per primary ionization.

PLATZMAN: From data at high energy?

POLLARD: Well, yes. There is a lot of work. I cannot quote them all from memory, but the first one who comes to mind is Williams and Terroux, who did a lot of work with beta rays for this express purpose. They set the expansion to catch not the separate droplets, which is what C.T.R. Wilson did and has been done since, too, but actually to catch just a blob of primary ionization, and then they counted the number of blobs, and they tell the energy that they themselves worked out, in fact, the density of the gas, etc., and they know the stopping power. In that way you can estimate the number of electron volts that must go into primary ionization. Other work has been done by Beekman, Corson and Brode. All of this work, which was done between 1930 and 1940, agrees quite well. So it looks as though, if one can argue from gases to the liquid-solid combination of radiobiology, one can at least say that the average energy that is developed per release is 110 electron volts. This tells you how many primary ionizations there are. It does not tell you how many primary excitations there are, and it does not tell you a thing about the energy, this being an average. It is an average over a very wide range. It is useful in telling you the number of processes that must occur. I have taken the Bethe formula that is in the Bethe article, and you can write this down and calculate on this basis, but unfortunately you don't know where to chop it off at the lower end. Start off at 5 electron volts and chop off at 10 or at 15 and you will get a very different result according to where you chop it off. So that is why I was waiting for some information.

TOBIAS: I found some reports which approached the problem of delta rays in a somewhat different way from what is discussed here. Among others Symon (18) and Igo et al (19), have performed experiments in which they measured the fluctuation in ionization along tracks of particles, in a proportional counter. The fluctuations chiefly arise from secondaries, that is delta rays produced along the track with a distribution of energies. The ionization pulses collected and measured give a statistical pulse size distribution which is different from Poisson's distribution. The shape of the distribution can be predicted on the basis of theories of Landau and others concerning the energy distribution of secondary electrons. Now accurate measurements of this kind could perhaps be used in the future to test the theories of delta ray energy distribution. It may be interesting to some of you to consider for example the pulse height distribution obtained by Igo, et al, on protons. (See Fig. 1.)

PLATZMAN: How many primary events are there?

TOBIAS: Each proton makes about 100 secondary electrons in its passage through the proportional counter.

FANO: Experiments of this type do not contribute important information regarding the energy distribution of secondary electrons. It is known that this distribution follows a $1/E^2$ law for E much larger than the binding energy of the atomic electrons. The fluctuations of ionization observed in the experiment and considered by the Landau theory just discussed arise from collisions with values of E sufficiently large for the $1/E^2$ law to hold. Hence any verification of the Landau theory merely confirms what we know but contributes nothing to what we don't know, namely to the distribution of <u>small</u> energy losses.

TOBIAS: I assumed that at present you have to make assumptions even in the first part of the delta ray distribution, where the delta ray energy is low,

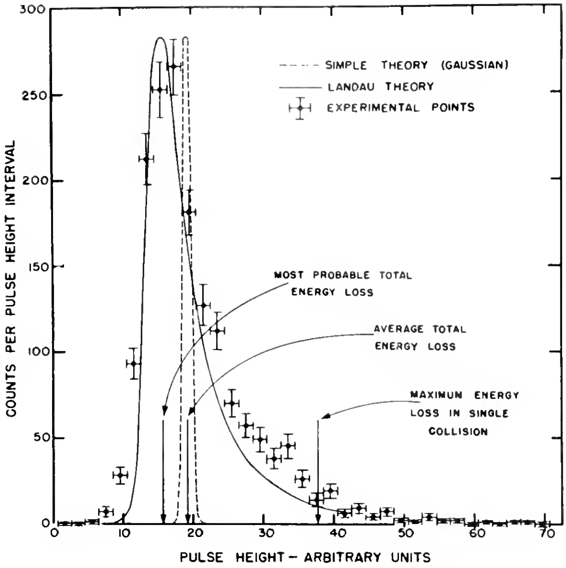

Fig. 1. (reproduced from Igo et. al., Phys. Rev. 89, 879 (1953)). Frequency distribution of energy losses of 31.5 Mev protons traversing 3/4'' proportional counter. Histogram of experimental points shows standard deviation and channel widths. The theoretical Landau distribution is computed from Symon. The dashed curve is a Gaussian distribution based on ion pair statistics. The ordinate is counts per pulse height interval.

and that the work I mentioned was the first real experimental test.

FANO: Small energy losses enter in the theory only through their contribution to the stopping power; there is another correction which is called the Blunck-Leisegang correction which you can put in if you want to, but does not amount to much.

POLLARD: The proportional counter is a very nasty test to use in this region. You are just above the ease of detection against noise if you use 500 ion pairs. When you get down below that it is very hard to use. That means you have to have high multiplication factors. Immediately there begins to be the question of where the particle goes through the counter, and all the other things that make it hard to work with begin to come in. So I would feel there would be additional experimental uncertainty that I personally would worry about.

FANO: I thought the proportional counter with a few kilovolts had been used by lots of people.

POLLARD: It is not easy.

FANO: No, it is not easy, but there is all that work on tritium, especially by the Glasgow people.

BURTON: Was a number of proportional counters operating simultaneously in this instance?

POLLARD: No, it is just one, the pulse height analyzed from one.

BURTON: One could visualize a situation where the track goes down a tube. You have one central electrode and a series of circumferential electrodes with a corresponding number of proportional counters operating simultaneously. The electric circuits may be fixed so that the only time they can operate is when they are all operating. In this way noise effects may be eliminated. The essential idea was used by Libby (20) in some of his work on Carbon 14. He eliminated the noise level by getting only the simultaneous count. This would be an interesting technique to be used in the case under discussion.

TOBIAS: The measurements I mentioned were done on protons.

BURTON: I might note that the difficulty with the experiment I proposed is that the results would be very important but that the data would be unfortunately numerically unimpressive when measured in terms of man-days required for their production.

MECHANISMS OF ENERGY DEGRADATION AND CHEMICAL CHANGE: EFFECTS OF SECONDARY ELECTRONS

John L. Magee

In this conference we are trying to form a picture as concrete as we can of what happens when high energy radiation is absorbed in matter. I am going to be speaking generally of the case of water, just as Dr. Platzman did yesterday. I don't mean to offend anybody who likes to emphasize the importance of other media, but we have to limit the discussion. The general picture is something like this: for fast particles primary events are rather widely spaced. No one would argue that there is any effect transmitted directly from one of these primarily affected regions to another. There will be a distance of several thousand Angstroms between successive events for a very fast particle, say a half-million-volt electron. On the other hand, for a very low velocity primary particle, such as an alpha particle, primary events are quite closely spaced and it is generally conceded that the effects overlap. So we have essentially these two extreme cases: one in which a column is formed, and one in which there are isolated events.

Yesterday Dr. Platzman was telling about an attempt to explain what happens to an ionized electron in water. How far does it go? In the way of a detailed picture there is only one thing we have had in the past of which I know -- that is, the only people who have been willing to stick their necks out and give a detailed picture were Lea and Gray (1). They gave a detailed model for the distribution of radicals in space, and we talked about this yesterday; namely that the H_2O^+ is left behind along the columns or at the centers of isolated primary events and that H_2O^+ dissociates to form H^+ and OH. Then, of course, there is electron capture which gives an H atom plus an hydroxyl ion. The idea was that this capture took place at some distance away. This distance, the only value that I have seen given frequently, is 150 Å, the idea being that there is a sort of Gaussian distribution

$$n_H(r) \propto \exp(-r^2/b^2)$$

and the parameter b is about 150 Å. Here $n_H(r)$ is the number of H atoms formed per unit volume at the distance r from the center of the affected region.

Essentially the electron gets away to a distance of the order of 150 Å. This is the thing that Dr. Platzman was reaching for yesterday, except that he overstretched, according to his own statements, and wanted the electron to go further.

BURTON: Let us get this straight. I thought Dr. Platzman was talking about electrons which came out with about ten volts of energy, and you are talking about electrons which come from the primary column.

MAGEE: All electrons quickly get down to the ten volt region. Dr. Platzman was talking about the mechanism which gets the slow electrons away.

BURTON: Was he talking about electrons from the secondary process or the primary?

MAGEE: He stated that he was talking about a specific event, which formed only one electron. Isn't that what you were talking about?

PLATZMAN: Yes.

BURTON: That was an isolated thing he was talking about, and I did not think he was tying it up to this geometrical picture that you have been developing.

MAGEE: Well, I want to make this discussion concrete. As nearly as I can tell, this is the only way to get this picture. There are no real calculations on this parameter $b \approx 150$ Å.

POLLARD: 150 Å would be the range of a delta ray, or something like that.

BURTON: That is the way I get it.

POLLARD: It is much too high.

MAGEE: It won't apply. The picture we were given yesterday was for an isolated event. Dr. Platzman calculated 50 Å.

BURTON: For 10-volt electrons.

PLATZMAN: To thermalization, not to capture.

BURTON: The 150 Å distance is for delta rays, if I understand correctly.

FANO: No, the delta ray is very short usually as compared to that.

POLLARD: How does the 150 Å get to be that big? I will take 50 Å but I cannot see 150 Å.

MAGEE: I don't know that this has ever really been described in detail.

BOAG: It comes from two sources: (A) measurements of the initial separation of ion pairs in a gas, as seen in cloud chamber photographs (2), scaled down in the ratio of the densities of water and gas, and (B) saturation measurements in compressed gases interpreted by the Jaffe theory (3). Neither method is direct, but both yield about 150 Å.

MAGEE: That is, as I said, what has been generally believed.

PLATZMAN: I think it is more of a pious hope than a belief.

FANO: It is a figure applying to gases reduced in proportion to density.

MAGEE: At Notre Dame Samuel and I have been trying to embark on a program in which we would get as much evidence from different points of view as possible on this picture, and we have not invested a great deal of time or energy in this particular type of calculation. We would like first to rough-out the whole picture and then sharpen it up where necessary. That is what I am going to try to do today.

First let me call your attention to the fact that there are several lines of evidence which bear on this picture. In the first place you have theoretical calculations, such as Dr. Platzman was telling us about yesterday. Then there are experimental results. There are physical experiments and chemical experiments, and these all bear on the spatial distribution. We have thought about all of these things.

First let us review. Let's mention the theoretical evidence, and go back to the primary event in which there is only one electron. I started thinking about this several years ago, and so I was quite interested in the problem that Dr. Platzman was discussing yesterday. I didn't want to do such an elaborate calculation, and yet I wanted to get an approximate result. As a matter of fact, I must say at that time I thought the electron got quite far away, and if you remember a paper (4) that Dr. Burton and I wrote, we were discussing electron capture as a competition of various processes. I thought the electron certainly got free of the coulomb field, and I just wanted to get a rough estimate of how far it went, and so I looked in the literature and got experimental data on electron scattering and capture. Brüche (5) had reported scattering data and Bailey and Duncanson (6) had reported energy loss data for slow electrons in water vapor. Doubt has been cast on the validity of these data even for the gas phase. I used it anyway and calculated the distance that the electron would get away, saying that it would move in such a way that $\overline{r^2} = nL^2$, where r is the distance of the electron with respect to its parent ion, L is the scattering mean free path, and n is the number of collisions which have occurred. For n we can take $n = vt/L$ where v is the velocity and t is the time. If the coulombic energy is neglected, the only change in electron energy is due to inelastic collisions, and we can say $-\frac{dE}{dn} = \lambda E$, where λ is the fraction of energy lost per collision.
Substitution for n gives

$$-\frac{dE}{dr^2} = \frac{\lambda}{L^2}E$$

and integration, for constant parameters λ and L gives

$$E = E_0 \exp(-\lambda \overline{r^2} / L^2)$$

if the electron starts with E = 10 ev, it gets down to E = 1/40 ev (thermal energy) when

$$\overline{r^2} = \frac{L^2}{\lambda} \ln 400 = \frac{6L^2}{\lambda}$$

$$\text{For } L = 2\ \text{Å},\ \lambda = 0.04:\ (\overline{r^2})^{\frac{1}{2}}_{th} = 24\ \text{Å}$$

This calculation is obviously inconsistent, since at 24 Å separation the coulombic energy is much higher than thermal energy. Samuel and I (7) have made a similar classical calculation in which we took into account the coulombic field, and, of course, the electron does not get away quite as far in this case.

ONSAGER: This calculation is classical in what respect?

MAGEE: The electron is taken as a point charge, and I will remind you of a fact that Dr. Platzman mentioned yesterday. The electron starts off with about 10 ev and its de Broglie wave length is about the size of a water molecule, but before the electron drops to thermal energy, its de Broglie wave length covers several molecules. Actually the electron is colliding with several molecules at once, and so a condensed gas model with a constant mean free path doesn't have any particular meaning.

FANO: With regard to the Bailey-Duncanson work, the cross section of the gas phase water molecule, is going to be much larger than geometrical because of the dipole, and that shortens the mean free path.

MAGEE: You think the cross section of the gas phase is much bigger than it would be in the liquid? Is that the idea?

FANO: Yes.

MAGEE: Of course, there are any number of reasons one cannot believe a calculation such as Samuel and I made. However, the result came as a surprise to me, so I began looking around for other evidence which bears in one way or another on this result. I would not believe such a calculation on its own merits. In fact, I don't know how to make a calculation I would believe. I think I would agree with Dr. Platzman that you can only calculate the order of magnitude. He obtained 50 Å which, incidentally, was a confirmation of capture, because at that point the electron had already been thermalized, but the coulomb field was over twice as great as kT and the electron in about 10^{-12} of a second would get back due to the influence of the field.

PLATZMAN: It is only fair to say, however, that we disagree on that.

MAGEE: All right.

PLATZMAN: Dr. Magee has made a definite theory based on a certain model, and we should understand two things: first, how his theory develops from the model, and, secondly, the foundation of the model, keeping the two separate.

MAGEE: I should like to emphasize that this calculation is of interest as a classical limit. One calculates limits to get ideas, and of course, may come out with the correct order of magnitude.

BURTON: What is important in this model is the fraction of energy transferred on each collision. That is very important.

MAGEE: There is another factor, the main free path between collisions, and that is the thing which could get the electron to large distances. If there is a big main free path, the electron will get away.

ONSAGER: May I ask a question? What radial distribution do you and Samuel compute for the thermalized electrons?

MAGEE: Our calculation is not that elegant. We only calculated for an electron which had an average value of r^2. It is a very crude calculation, but it does indicate the classical result. It is the one line of evidence which first led us to believe that there was a possibility that the parent ion could do capturing, due to the fact that there are very strong inelastic collisions and excitation of thermal motions. I would certainly not say that this calculation would indicate that this process is the actual one which happens. As I said before, at first I am trying to put together a picture as furnished from a number of lines of evidence, and the main thing I am going to emphasize is chemical evidence.

KAMEN: You are assuming that your positive charge is staying where it was formed?

MAGEE: Yes.

FANO: Shouldn't we try perhaps to fix this other point about recapture? Dr. Onsager, didn't I understand from you yesterday (and it sounded quite the obvious thing) that the probability of recapture if the thermalization happens at distance r will be $\exp(-e^2/\epsilon rkT)$?

ONSAGER: Right.

FANO: If the value of ϵ is five, it is a distance of 100 Å that make the difference. Anything within 100 Å will have a high probability of recapture. Is this the right figure: if you put in $r = 100$ and $\epsilon = 5$, the exponent is one?

PLATZMAN: That is Dr. Magee's view. Is that correct?

MAGEE: I beg your pardon?

PLATZMAN: It is your view that this gives the order of magnitude.

MAGEE: No, I haven't used this. The situation here is that ϵ is a constant and there is all the time in the world. You don't worry about how long it takes the electron to get back. Isn't that right?

ONSAGER: That is true.

MAGEE: But if there is a 10^{-11} second time limit before the dielectric relaxes, the electron must move in sooner, or it is frozen out because the increase in ϵ weakens the electric field.

FANO: So you say it is probably not so.

PLATZMAN: At least I do not believe that, but I don't want to say anything about it now.

MAGEE: In other words, I would say if the electron does get to 150 Å, then before it can get back a significant distance the dielectric relaxes and freezes it where it was and you will, indeed, have the electron separated from the ion. I don't believe it ever gets far enough to do this, but I am just calling it to your attention.

I don't know whether all of you know about the experimental work of Gerritsen (8) on conductivity. I don't think it will be worth our time to get into a discussion of conductivity, but let me say just a word about it and show you some of his results. Let me call your attention also to the fact that now I am not talking about water, because experiments in water have not been done; but Gerritsen did some conductivity measurements in helium, argon, H_2 and N_2 under irradiation and calculated the quantity b which would fit into the conductivity result. You see, it has all the theory of conductivity coming into it, but the values of b I found very interesting. Results are shown in table III. All samples are liquids; "covered" and "uncovered" samples were used and I do not know why different results were obtained for the two cases.

TABLE III

PARAMETER b FROM GERRITSEN'S CONDUCTIVITY MEASUREMENTS

Substance	Temperature (^{o}K)	b (Å)
He covered	1.3	470
He covered	3.98	550
uncovered	3.98	750
A uncovered	88	810
H_2 covered	20.4	16
uncovered	20.4	18
N_2 covered	77	7.5
uncovered	77	25

The way we interpreted these results when we first saw them was that molecules have an effective mechanism for dissipation of electron energy. The electrons get quite far away if they have positive energy and there is only minor dissipation due to elastic collisions. But if they have in addition any other mechanism of dissipation, apparently the evidence seems to be that they are trapped in a lot closer. Davidson et al (9) report that they cannot get any conduction in liquid N_2 at all.

These conductivity results cannot be understood without careful analysis, and I am just calling your attention to them. They furnish a line of evidence which I think indicates that energy dissipation in molecules may be quite effective in stopping electrons leaving positive charges.

Now I will come to the part I think we should discuss most thoroughly, and this will probably be of more interest to biologists. It is the chemical evidence. Samuel and I had in mind, when we started looking at all of this picture, that we wanted to put together a radical diffusion model for chemical effects of radiation on water. For this we wouldn't really need to specify the radical formation mechanism.

I am not really tying all of this together as a complete and continuous theory. It is just a sort of fragmentary discussion. For example, what I am telling you now does not depend on the previous electron capture discussion as a foundation.

I hesitate to talk about water with so many radiation chemists in our midst, but with their help this discussion can turn out to be quite profitable. Let's take, for example, the effect of gamma rays on water. You remember that in the case of high-energy gamma rays, most of the primary events which will take place will be formed isolated from each other. I don't think anybody will argue that any effects are transmitted directly from one primary event to another. The effects of irradiation can be summarized this way: water decomposes according to two mechanisms, part of it giving what is called the "forward reaction", with products H_2 and H_2O_2 and the other giving the "radical reaction", with products H and OH (10). Later Dr. Allen will tell you something about the chemical evidence of this. I really hesitate to discuss it in his presence, since he was the originator of this set of reactions. In equation form we have

$$H_2O \rightsquigarrow \tfrac{1}{2}H_2 + \tfrac{1}{2}H_2O_2 \qquad \text{F}$$

$$H_2O \rightsquigarrow H + OH \qquad \text{R}$$

where the symbol $\rightsquigarrow$ means "under the influence of high-energy radiation gives".

These reactions can be separated by the introduction of scavengers into the medium, which are very effective in reacting with all of the radicals which are formed. You will find, even if there is a high concentration of scavenger, you get some of the F reaction. It has also been demonstrated, with isotopes (11), that the H_2 and H_2O_2 comes from the water. It does not come from any kind of solute in the water, even when you are scavenging the radicals, but comes directly from the water.

It seemed attractive to us to put together a model in which you get the same number of radicals per unit energy regardless of the type of radiation - gamma, tritium-beta, or alpha - and a radical distribution depending on the ionization density of the radiation. For gamma radiation, it is known experimentally that 20 per cent of the radicals must go into the F reaction, and around 80 per cent into the R reaction; while in the case of alpha, of course, something like 90 per cent must go into the F reaction and only 10 per cent into the R reaction.

It looked as if there were a possibility to explain these facts on a geometrical basis, i.e. with the use of radical diffusion only, and we started out to do just that. I will indicate how the theory goes and apply it to the case of gamma rays.

You see how this has to work. For the case of the gamma rays, a typical primary event will form several radical pairs. Let's say they are formed in some kind of a region which I will indicate as spherical. We will say this sphere is drawn about the center of an event.

FANO: I should like to take issue with your saying a typical primary event has several radical pairs. The typical primary event has but one radical pair. Most frequently a primary event has but one radical pair. It is the usual misunderstanding that a typical ion cluster in air has three ion pairs. Three is not typical.

ALLEN: I think the point is that the fraction of radicals which are formed in these isolated pairs is not very large.

MAGEE: Well, let's go on with this. I want to get the model out before you first, and then you can tear it to bits. You understand that if I were following the Lea description I was telling you about, I would have said the thing to do is to take the OH radicals as in a Gaussian distribution, say with one *b* parameter, and the H atoms as in another Gaussian distribution with another *b* parameter.

BOAG: Both the H and the OH radicals are assumed to be in Gaussian density distributions having maxima on the axis and differing only in half width. However, some of the OH's are formed along the tracks of delta rays.

MAGEE: We have one primary event which forms, say, three OH's. Take the three as shown in figure 2d. The primarily affected molecule is not necessarily in the center of the sphere. The ionizations take place rather quickly and leave the OH's close together. The H's are in the vicinity as shown.

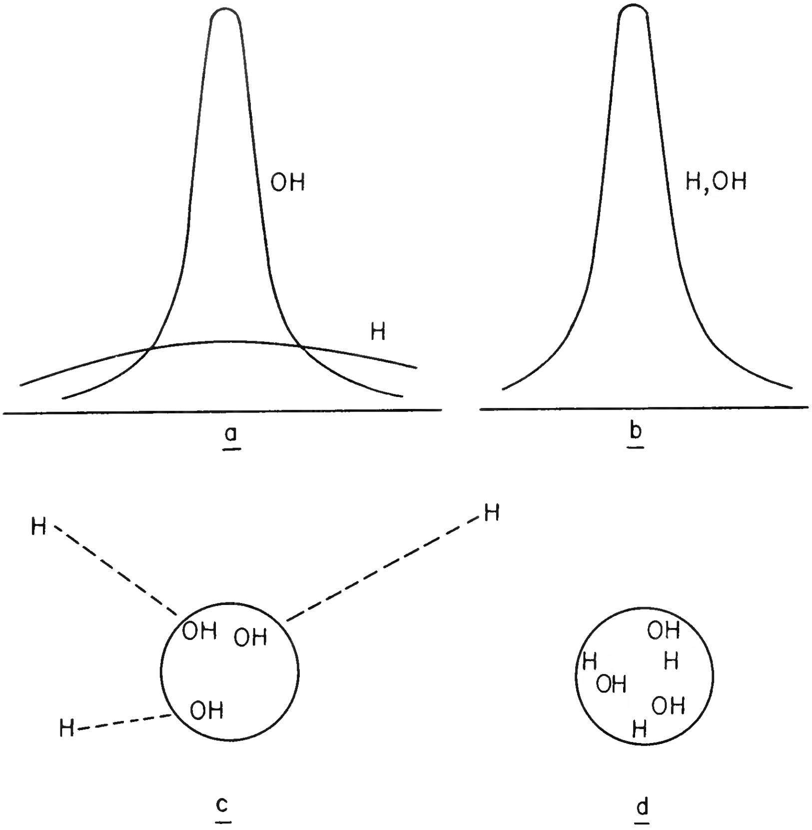

Fig. 2. (a) Distribution of radicals around track as envisaged by Lea.[1] (b) Distribution of radicals around track as envisaged by Samuel and Magee. (c) Typical spur according to Lea-Gray model. (d) Typical spur according to Samuel-Magee model.

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[1] - from D.E. Lea, Brit. J. Radio. Supplement 1, 59 (1947)

We were influenced by the considerations which I have told you about, and we said what actually happens is, of course, that the electron gets back. A highly excited H_2O molecule is formed by the electron capture and then it dissociates. The H atom, having a considerable amount of kinetic energy, will get several molecular diameters away, and so the H atoms are formed more or less randomly. We decided to take all radicals formed, completely at random, in such a small volume as shown in figure 2d. That is the picture we have been working with: all H and OH radicals are distributed completely at random within some kind of a volume. It should be understood that all of the previous discussion about the radical formation from excited H_2O molecules just provides the only mechanism I can think of, but we still have the radical diffusion picture to build up. Regardless of the details of this mechanism, it is of some interest to see whether it gives anything reasonable or not.

I shall make this development as brief as possible. The radicals are all confined within a spherical region of radius r, where r increases with time according to $r^2 = \lambda u_R t$ in which λ is a distance of the order of a radical jump distance; u_R is a velocity, and t is the time. We shall not define precisely what is meant by r, but it is clearly something like the square root of the mean square radius for the diffusing radicals.

The random motion of the radicals is actually a sort of confinement. If we say that N radicals are within the volume $v = \frac{4}{3}\pi r^3$, the rate at which they disappear by mutual reaction is

$$-\frac{dN}{dt} = k \frac{(N)^2}{v} v$$

where k is the reaction rate constant. Substitution for v in terms of r, and r in terms of t yields:

$$-\frac{dN}{dt} = \frac{3k \;\; N^2}{4\pi\,(\lambda u_R t)} \;\; 3/2$$

This equation integrates to:

$$\frac{N}{N_o} = \frac{1}{1 + \frac{2k\,N_o t_o}{v_o}\left(1 - \frac{r_o}{r}\right)}$$

where the initial conditions $v_o = \frac{4}{3}\pi\, r_o^3 = \frac{4}{3}\pi\, \lambda^3 u_R t_o^3$ have been inserted.

At the time $t = \infty$, the fraction of radicals

$$\frac{N\infty}{N_o} = \frac{1}{1 + \frac{2k\,N_o t_o}{v_o}}$$

remain uncombined. The fraction $1 - \frac{N\infty}{N_o}$ have combined with each other.

Thus a certain fraction of the radicals will combine and a certain fraction will get away. This is exactly the kind of separation into two classes we wanted in order to explain the F and R reactions. There is a distribution between the two processes; it depends on the magnitude of the parameter $y = \frac{2kN_o t_o}{v_o}$.

I think probably the most efficient procedure is just to summarize our calculations. For details you can refer to the paper by Samuel and Magee (7). We had to put in a distribution function for the number of radicals formed in primary events and definite values for the r_o's. We don't have good information as to what the actual distribution is of N_o for the actual events of ionizing particles, but the calculation does not turn out to be too sensitive to that. If you adjust parameters to obtain the observed value, say, for what fraction of radicals goes the F reaction and what fraction goes the R reaction for gamma rays, you find that the

r_o you have to take has to be rather small. For example, for a group of six radicals it has to be about 10 Å.

It might be worthwhile to examine this situation in a rough way, since it will not take long. The fraction of radicals which combine during the expansion is $\frac{y}{1+y}$, but all of these are not observed as taking part in the F reaction, since the combination of H and OH produces water again. The net fraction which produces H_2 and H_2O_2 is $\frac{\frac{1}{2}N_o - 1}{N_o - 1} \; \frac{y}{1+y}$. The fraction of radicals which are <u>observed</u> as entering the F reaction is, therefore, given by

$$\frac{\dfrac{\frac{1}{2}N_o - 1}{N_o - 1} \quad \dfrac{1}{1+y}}{\dfrac{\frac{1}{2}N_o - 1}{N_o - 1} \; \dfrac{y}{1+y} \qquad \dfrac{1}{1+y}}$$

If we take $N_o = 6$ and equate this quantity to $\frac{1}{4}$, which is approximately the observed ratio, we find $y = 5/6$.

With relationships already introduced we can write

$$y = \frac{3k\,N_o}{2\pi r_o \lambda\, u_R} = \frac{9k}{\pi\, r_o \lambda\, u_R}$$

The quantity k is the reaction rate constand and we take for it

$$k = \pi\,\sigma^2 u_R$$

where σ is a collision radius for a radical pair. At this point one could object violently to the use of the same σ and u_R for both H and OH radicals.

FANO: Doe what you are doing amount to something like an estimate of the diffusion coefficient?

MAGEE: No, this is the reaction rate constant. I assume that the radicals will react as often as they can find each other. The cross section is, $\pi\,\sigma\;2$.

FANO: u_R is the thermal speed?

MAGEE: Yes.

FANO: I think any estimation of the diffusion coefficient based on this formula will tend to give you something quite off in speed and --

MAGEE: The point is that in the quantity y you have speed upstairs and you have speed downstairs and the two cancel out and you don't put a number in for speed. The reason I would not worry about the speed is because the motion, as I visualize it, is like this: a radical is in first one position and then another. It moves by jumping between pairs of positions. It does not jump with thermal velocity, but it jiggles around in each position a certain number of times. You don't know how long it jiggles around. Then it moves over and jiggles again a certain number of times, and so on. It has to wait until it gets thermal activation before it can change position.

ONSAGER: It is very difficult to develop a full-fledged kinetic theory for diffusion in liquid and particularly perhaps in water. On the other hand, I don't believe it is really necessary because all coefficients of diffusion are reasonably small.

MAGEE: You can do it if you like, but I --

ONSAGER: I don't want to. I rely on experience with more orthodox molecules.

MAGEE: As a matter of fact, it is certainly true that nothing about the diffusion coefficients or reaction rates are known for radicals I don't know any experimental evidence at all. But I want to estimate this quantity y.

ONSAGER: Let's see what you have done.

MAGEE: So far I just have k. Now we can substitute and get

$$y = \frac{9\sigma^2}{r_o \lambda}$$

The reason I am doing this in such detail is to give everyone a chance to object. I think that lambda and sigma have to be about the same magnitude, and so we can write

$$y \approx \frac{9\sigma}{r_o}$$

POLLARD: What do you take for sigma and lambda?

MAGEE: I have taken 2 Å for sigma and the same for lambda. For $y = 5/6$ this gives $r_o = 22$ Å. If a Gaussian distribution for radicals is used instead of this model I have described, the b value for the spur containing six radicals turns out to be about 10 Å. This calculation is described in the paper by Samuel and myself (7).

BURTON: In this model your assumptions are substantially equivalent to saying, in terms of chemistry, that the rate constant of the reaction giving H_2 is equal to the rate constant of the reaction giving H_2O.

MAGEE: That is right.

BURTON: We all feel instinctively that is not so.

MAGEE: We have started to look into a number of such questions. Of course, it is very discouraging to try to make *a priori* calculations as to what these rate constants are, but in this particular case there are factors which tend to balance out. That is, I don't feel too bad about putting the k's for H_2 and HOH the same. However, I would think that the HOH might be a little faster.

BURTON: If you put them the same, that is equivalent to saying quite apart from the σ value, that the λ value is the same, and that I know is not true. If you consider the H_2 and the H_2O_2, that is equivalent to saying that the λ value for H and OH are the same.

MAGEE: It is the parameter y that comes in.

BURTON: That is a rather important point. About two years ago in this conference we pointed out that in this forward reaction, it is only a matter of convenience to make the assumption that H_2 and H_2O_2 are formed in equivalent amount. We felt at that time, and we know very definitely now, that the yield of H_2 in the forward reaction is not the same as that of H_2O_2 in the forward reaction.

MAGEE: The only trouble is I haven't seen any improvement that I think I would like to discuss at this time. There are so many things to consider. When you start to think about it you don't want to improve one thing and leave something else just as important neglected.

ALLEN: I think Dr. Burton's point is important. On this theory, outside of the details, the general picture is that these radicals are uniformly distributed in a region from which they diffuse out, and it is hard to see how this can give you anything very different from having the amount of hydrogen formed pretty close to the amount of peroxide formed.

MAGEE: It will be about the same.

ALLEN: The evidence is becoming increasingly clear that the peroxide yield of gamma rays is about twice the yield of hydrogen, which is quite a big difference. The most obvious way of explaining this would be to go back at least partially to the old Lea picture and say that hydrogen atoms are more widely distributed to begin with then the OH radicals.

BURTON: Not necessarily. That view represents an over-simplification. All you have to do is note that the λ values are different.

ALLEN: This may not be the only possible explanation, but it is the way that first comes to mind.

MAGEE: Let me call your attention to the fact that there is just a 50 per cent -- or what difference do you have for the H_2 and the H_2O_2?

ALLEN: I think with gamma rays the H_2O_2 yield is about twice that H_2 yield. For rays of high ionization density, the factor may be even larger.

MAGEE: Well, there cannot be as much assymetry as having all of the OH in a little sphere and the H in a sphere ten times as big. That makes a tremendous difference, whereas there is only a small difference. One distribution is about the same as the other one, you see, in this case, and you may have a little difference in the rate constants and such things.

ALLEN: Consider your $N\infty/N_0$. You want this to come out twice as big for one of these as for the other.

BURTON: What Dr. Magee is doing is presenting a theory which distinguishes between the R reaction and the F reaction. There is a nuance here in that the F reaction is not the same for H_2 and H_2O_2, and that nuance can be treated in one of two ways: to have the hydrogen atoms a little further out, which is far inside the distance that we think of in the Lea-Gray picture, or to have them diffuse with a different mean free path. Either one of these would explain this nuance. But what he is trying to do is to explain this big ratio. Is that correct?

MAGEE: That is correct. For example, if you put 150 Å as r_o you find about one per cent recombination. You would have to change factors quite a lot before you can account for the observed F reaction. The k has to be an impossibly large value before there can be such a big radius. The reason we liked to choose these little spheres is because it fitted in with the idea of radical pair formation by a single molecule. If I say the electrons are captured and H is formed away from the parent ion -- I mean at a moderate distance -- I cannot understand why they are formed at all, because I think if they had stopped at a moderate distance they would come back. It is an all or none effect, I believe. They either have to come back or get away entirely, as Dr. Platzman says. I would agree with him, if they can get 100 Å away, they may be able to go a million. That is the way it looks to me. I cannot see any appreciable asymmetry. So it seems to me they must be captured.

PLATZMAN: Dr. Magee does not contend that this is going to give all the fine details. This is, as far as I know, the first real attempt to get kinetics out of the elementary processes. No doubt it is wrong in detail along the way, but we have to get the final picture, and it can still be very important even though some of the details are incorrect.

MAGEE: I don't have a great deal more to present. I am just going to say that we have taken into account the distribution of N_o. Actually we took several trial distributions and calculated the correct ratio of $G_F/(G_F + G_R)$ for gamma rays, as I said. We decided that a test would be to calculate for tritium-β, since the average primary event spacing is more like 150 Å and all the reaction does not occur before the spheres start overlapping. So part of the tritium-β effect is due to the isolated events, and part of it is due to the overlapping of neighboring events. We calculated this using the same N_o distribution and using the same constants. The ratio $G_F/(G_F+G_R)$ turned out to be 0.32 for tritium, whereas it had been 0.23 for gammas.

BURTON: I don't know whether it is clear to everybody what you mean. What Dr. Magee means is that Ghormley and Allen (12) did some work on tritium water, and the radiation was the beta emission from the tritium. It is to this experimental situation that the calculation applies.

ALLEN: He is referring to the more recent and much better work of E.J. Hart (13).

MAGEE: It is a self-irradiation of tritium water.

GARRISON: I should like to bring up a point regarding the HOH reaction. The total radicals observed either as H, OH, H_2 or H_2O_2 should vary with the specific ionization, according to this picture.

MAGEE: Yes.

GARRISON: But Hart found that this is not the case.

MAGEE: I don't know of any very clear-cut results along that line.

GARRISON: I don't think it has been completed as yet. In the work he did with polonium alphas forming gases with tritium betas and cobalt gammas he found that the total number of radicals observed as H, OH, H_2 and H_2O_2 was a constant.

MAGEE: In other words, no H_2O formation from the radicals seems to be in the picture.

GARRISON: No, the HOH reaction is either the same or it does not occur in these cases.

ALLEN: Let's get this straight now. With polonium alphas you have a G of about 1.8 for peroxide and hydrogen and the G for the radical is very small.

BURTON: If we don't let Dr. Magee present the end of this thing we won't know what we are talking about. He is pretty close to the end. Let's have the entire picture.

MAGEE: There are two numbers that I have to give. These, of course, assume that radicals formed in the R reaction remain free to be picked up by scavenger. The other radicals are distributed equally in the forward reaction and in the reaction forming H_2O. We fitted our parameter y to agree with gamma rays and then we calculated results for the tritium -β case using a particular average inter-event distance. The calculated and experimental values are given in table IV.

TABLE IV

CALCULATED AND EXPERIMENTAL VALUES FOR THE RATIO G_f/G_f+G_r

	Calculated	Experimental
Gamma Rays	0.23	0.21 Hart [a] 0.25 Hochanadel [b]
Tritium-β Rays	0.32	0.30 Hart [a]

a. J. Phys. Chem. 56 594 (1952)
b. J. Phys. Chem. 56 587 (1952)

I am essentially through now. What I have tried to give you is the general picture, and of necessity I have left out a great many details, so that it may not all be clear, but I would appreciate any comments and discussion you may have.

BURTON: Do you have values for alphas, too?

MAGEE: The alpha case is different. If you have a column you have a distribution described by two variables instead of three. The equation for the fraction of radicals remaining uncombined during expansion is

$$\frac{N}{N_o} = \frac{1}{1 + B \ln X}$$

where B is a constant and X is the expansion ratio of the column, i.e. as compared with its initial volume. Thus in an isolated column, all radicals will combine as X approaches infinity. However, there is rapid reaction only at first, and then radical recombination occurs very slowly.

ALLEN: I should like to make a remark or two. I think on the present picture the size of the region containing the hydrogen atoms is much smaller than 150 Å, something which you can also conclude simply from the dependence of the molecular hydrogen yield on the ionization density. If you have a particle track with clusters strung along it, then as you increase the ionization density these clusters will start to coalesce, and as the clusters coalesce the yield of molecular product will increase. From the rather fragmentary information available, it seems clear that the hydrogen yield does not greatly increase until you reach an ion density corresponding to that of an electron of the order of 3,000 or 4,000 ev. If you put in the numbers for the average ionization density and assume a random distribution of these clusters along the track, it is clear that the diameter of these groups of radicals cannot be much greater than 10 or 15 Å.

The point I was making is that the radical distribution picture may be obtained pretty well inductively rather directly from the experimental data, as I discussed at the Faraday Society meeting (14). It is very nice to find that Dr. Magee's more theoretical treatment is in agreement.

Another point is that if the peroxide yield is greater than the hydrogen yield it will not be possible to compare these numbers 0.23 and 0.32 very directly with experiments, because the experiment refers to the hydrogen yield; and in the case of tritium betas particularly, I think there is some evidence that the peroxide yield may be several times greater than the hydrogen yield. It is a little hard to know what number to compare with this 0.32, since it is based on a theory which does not take into account this difference between the hydrogen and peroxide yields.

FANO: I have been thinking at various times about recombination-diffusion theories. I learned that it is very convenient, in discussing these problems, to keep in the forefront a very few theoretical facts. The main fact is this: if two particles start diffusing at a distance r from one another and if they have a joint collision radius σ, their probability of ever colliding amounts to σ/r. If their probability of combination upon collision is p, their total probability of combination is $p\,\sigma/r$. If there are scavengers around, which may capture one of the two particles prior to its colliding with the other, the probability of collision follows the law $\sigma/r \exp(-r/a)$.

If the particles are ions pulled by an electric field E in opposite directions at an angle with the initial separation of the ions, their collision probability is $(\sigma/r) \exp\left[-\frac{eE}{RT} r\,(1+\cos\theta)\right]$ This formula leads to Jaffe's theory, of one takes $\sigma \doteq e^2/kT$ and integrates over the distribution of initial separations in a column of ions.

In all these formulas the element of primary importance is the ratio σ/r. The large value of this ratio for small values of r, nearly as small as σ, may give the mistaken impression that recombination is important only for particles that happen to start in close proximity. This is not necessarily time, because the chance of starting at large distances may be very great. If the probability σ/r is multiplied by a volume element $4\pi r^2 dr$, large values of r clearly give an overwhelming contribution. Even for a linear (or columnar) distribution, σ/r is multiplied by dr and, upon integration, the large values of r would give a logarithmically infinite contribution if they were not discriminated against by scavenger action, field separation, or other parasite effects.

MAGEE: In the case I was discussing, a chemical scavenger was present to eliminate the possibility of a columnar effect.

FANO: It depends on how effective the scavenger is.

ALLEN: There are scavengers which work from 10^{-6} molar up to 10^{-1} molar. For all this range of concentration the same yield is obtained.

FANO: If there are scavengers which suppress any large columnar effect, then this must be taken at face value, that you must start with r of the order of 10 Å. Otherwise you cannot get yield like that 0.2 or 0.3.

ALLEN: One of the lines of evidence on the size of these regions concerns the fraction of radicals which escape; another is this business of concentration of scavengers, which gives the same result regardless of concentration over a wide range; and the third is the variation of the molecular yields with ionization density of the radiation. They all appear to lead to something like 10 Å.

KAMEN: I think for some of us that it is important to make a point about the difference between Dr. Magee's theory and the older ideas, because everybody has been entertaining the notion that you make the ion-pair first and then you make the radicals from the dissociated ions. Now what Dr. Magee is saying is that you have no ionizations, and, therefore, there is no meaning to assigning an energy value, like 30 ev, for the work required to produce an ion-pair in liquid water.

BURTON: Excited molecules, no matter where or how originated, can be considered from the point of view of whether they contain enough energy to give radical pairs. The theoretical minimum that is required to give you a radical pair in the case of water is about 4.5 ev. Thus the theoretical maximum G for decomposition is 23, but it is evident that some excited molecules have far in excess of the energy required to give a radical pair, and some of them, for example those in low-lying triplet excited states, may not have enough energy to give a radical pair. All you can speak of is an average effect in a particular locale. In other words, if you can get n radical pairs there are enough sufficiently excited molecules there to give you n radical pairs. Where they originate is beside the point right now.

ZIRKLE: But you can get radical formation from excitations which are essentially primary energy transfers.

BURTON: If you really want to get complicated about this, then there is another thing that we have to consider, and that is that in these clusters there are also large numbers of excited molecules produced at a low excited state with a very high probability that such excited molecules may react with each other and produce reactions which are not radical reactions at all.

MAGEE: I have thought occasionally there is evidence that some of these excited molecules may be reactive. For example, there have been reported radical pair yields of up to 13 in certain cases. That is, I am talking about some of Dainton's results (15). He reports the highest value I have ever seen in water.

HOCHANADEL: That value of 13 radical pairs per 100 ev was based upon peroxide decomposition studies.

ALLEN: This was such a concentrated peroxide solution that the amount of peroxide was comparable to that of water in the solution.

BURTON: In such a case it is very easy to have a typical Stern-Volmer reaction and to have the excited molecules react with the hydrogen peroxide. I don't know how you establish the fact that it is a radical pair yield.

HOCHANADEL: Dainton and Rowbottom (15) determined the radical pair yield for gamma rays in liquid water by comparing the radiation yield in the radiolysis of carefully purified hydrogen peroxide with the quantum yield in the photolysis of the same solution. Assuming a primary quantum yield of 2.0 for dissociation of hydrogen peroxide into two hydroxyl radicals and also assuming that in both radiolysis and photolysis the rate is proportional to the square root of radiation intensity they calculated a yield of 13.4 radical pairs per 100 ev. This value is much higher than previously reported values which ranged around three radical pairs per 100 ev.

BURTON: Doesn't this experiment assume what is intended to be proved? It assumes that all the decomposition of the hydrogen peroxide you get is a result of a primary radical formation. Then Dainton calculates what the primary radical formation is in the case of the gamma-irradiated case on the basis of hydrogen peroxide that has been decomposed. However, there is an essential difference between gamma-irradiation and photon irradiation. In the case of photon irradiation, we deal practically exclusively with optically allowed transitions. Consequently, there is a good possibility that the only way the excited state so produced can make a contribution is that it decompose to give radicals; otherwise the excited states may disappear by fluorescence, for example, before anything else may happen. On the other hand, in the case of gamma irradiation a number of optically forbidden transitions may occur. Thus, the excited states may be quite resistant to emission of light as a method of degradation of energy. They may consequently survive sufficiently long to enter into radio-sensitization or straightforward metathetical reactions. Consequently, for the very high hydrogen peroxide concentration that I understand Dainton was employing there is a very high probability of reaction between excited water molecules and hydrogen peroxide molecules. It does not follow that his results really mean that he had this high radical pair yield. I don't say it is wrong. I simply say it does not necessarily follow from his work that he had these high radical pair yields.

ALLEN: I think the way I would put your point is that you may get excited states formed in the irradiation of water which normally disappear without giving any chemical effect. But if you have a fairly concentrated solution of some quite unstable molecule, such as hydrogen peroxide, the energy of these excited states may pass over to the hydrogen peroxide by excitation transfer, leading to its decomposition.

BURTON: Or have a Stern-Volmer reaction, but in either case under those conditions the excited H_2O is sufficiently persistent for one of those two reactions to happen.

LINSCHITZ: I don't know whether there are any stable, long-lived excited states of water at all.

MAGEE: I don't know of any experimental work on this. I know there is a paper by Niira (16), who calculated some low-laying electronic states of H_2O. He says that the HOH molecules, in a linear form, in a triplet state, is a metastable molecule which has an energy of about 2 ev higher than the ground state. It is an isomer of H_2O, a linear, triplet isomer.

PLATZMAN: Why isn't it formed in a Franck-Hertz experiment?

MAGEE: Possibly it is.

PLATZMAN: The Franck-Condon principle would not allow such a transition directly, but it might be possible to go up about 4 or 5 volts and then go down to such a state by rearrangement.

BURTON: That does not mean it lasts forever. Such an excited molecule may enter into chemical reaction and there are also other ways that it can disappear in water.

PLATZMAN: Should we say we all look upon this with skepticism and great interest?

MAGEE: I see no reason to be skeptical. I think it is rather certain that there is a stable triplet linear state of H_2O. The energy of the state is, of course, not well determined.

PLATZMAN: Do you think that if it does exist it could be important in kinetics?

MAGEE: I think it might be. Perhaps even in radiation chemistry. Such states can be formed by recombination of H and HO radicals and you may get them in great abundance.

PLATZMAN: Then pairs of these metastable molecules might give chemical reaction?

MAGEE: Possibly. I don't know what they do.

KAMEN: The impression that comes to me as an intermediary here is that it seems now to be rather stupid to look for an experiment to find out how much energy it takes to make an ion pair in water.

ALLEN: The question that has experimental meaning, at least in some connections, is how much energy it takes to make a radical pair.

PLATZMAN: At Oberlin I pointed out that the very concept of ionization is very vague in water (17).

KAMEN: Yes, it is beginning to percolate.

BURTON: There is a series of papers by Hart (18), for example, who has been using the term "radical pair yield" for a long time.

BOAG: The question I should like to have answered is whether the ejected electron in water returns to its parent ion or whether it becomes attached to another molecule some distance away. If Dr. Platzman is right, then there _is_ meaning in speaking of ion pairs in water.

BURTON: If there is meaning in speaking in terms of ion pairs in water, then this may be one of the few liquid cases in which this meaning survives. It becomes less probable in ammonia, and very improbable in a liquid like benzene, that there is any meaning in talking about ion pairs at all as being the source of chemical effects.

ALLEN: I think as to the meaning of ion pairs in liquids, it may mean something in the context of a theory, but if you look at it operationally it is very hard to imagine an experiment that could be directly related to this number. From that viewpoint it seems to hold no significance.

BURTON: There should be an operational difference. If what Dr. Platzman says is correct as compared with what Dr. Magee says, then these ions are formed and are persistent so far from each other that there are effects which should be detectible for H_2O^+ dissociating into H^+ and OH, and solvated electrons dissociating to give OH^- and an H atom remotely. These phenomena are so different that one might properly look for a suitable experiment by which they can be differentiated.

KAMEN: Let's be specific. What are these effects you are looking for?

BURTON: You have to think of what kind of an experiment can be done to find this.

PLATZMAN: That is exactly the problem, and at the present time no one is clever enough to think of an experiment that makes sense.

KAMEN: The next thing I want to say is what difference does it actually make to the radiation chemist as to whether this question is or isn't settled. Is it really important?

PLATZMAN: It might be a significant distinction.

KAMEN: It is important to know what the radical pair is, what the the distribution is, and whether the mechanism of radical pair formation is through recombination of ions or through direct excitation.

BURTON: The radical pair yield and the distribution of the radical pairs are the important things, not the radical pair yield by itself.

POLLARD: How do you know that radical pairs have any effect in biology? The statement has been made that it is much more important to know the radical pair yield than the ion pair yield.

KAMEN: Because that is experimentally something which you can measure.

POLLARD: If only ion pairs have an effect in biology, one is not interested in radical pairs.

KAMEN: There is some work by Read (19) purporting to show that the electrostatic effect produced by the separation of the electron, say in protein from its parent ion is such as could disrupt the molecule without intervention of the radical reaction.

BOAG: Read calculated that a radical electric field of the order of 10^6 volts/cm would be set up if two Gaussian charge distributions of opposite sign and different half-widths were superimposed in accordance with the Jaffe model. The region of high field is very small, however, and it seems unlikely that the Jaffe theory can give a true picture of the phenomena in a region only one or two orders of magnitude larger than molecular dimensions.

KAMEN: Was his error in the choice of the region over which it acted?

BOAG: Read's paper was mainly aimed at pointing out the difficulties and inconsistencies of the Jaffe theory when applied to liquids. Having shown that the calculated field strengths were so high, he concluded that the theory was badly in need of revision.

ONSAGER: Ions produced by charged particles, either alphas or electrons, have three chances to recombine before they get to the walls. The first possibility is that an electron recombines with its parent positive ion, a process which is much more probable if the electron can attach itself to a molecule first and form a negative ion. This type is known as "preferential" recombination. Secondly, the passage of a fast particle leaves a string of ionized atoms and molecules in its track; an electron can recombine with any positive ion in the same track and it is liberated in a favorable position to do so. This is known as columnar or "initial" recombination. Finally, the electron may recombine with a positive ion formed in any track. This is called "general" recombination. These three we have to deal with. I think most of you know these concepts, but maybe the terminology is variable and I am not taking any chances.

The theory of general recombination has been known for a long time, more or less. At low pressures it seems to depend on three-body collisions; the binary rate constant increases with the pressure. On the other hand, at very high pressures the rate constant decreases again because the ions have to find each other first, and the speed of that process is inversely proportional to the pressure (20). The optimum pressure depends on the ions and on the gas.

For the columnar recombination we have an old theory due to G. Jaffe (3). It is not an exact theory, but it ought to give the right orders of magnitude. In the absence of an external electric field, the recombination competes with diffusion in such a manner that the total number of ions surviving is inversely proportional to the logarithm of the time. An electric field helps to separate the ions in such a manner that a finite proportion of the ions will escape recombination forever, even from a track of infinite length, and those will be collected at the electrodes if they escape general recombination on the way. If we measure the current as a function of the field we can use Jaffe's theory to estimate the initial distance of separation of the ions. When the gas is dry air at high pressure, the electrons seem to get attached to the oxygen molecules fairly soon, and the initial distance in Jaffe's theory would be the distance at the time of attachment. From the fact that there is hardly any columnar recombination in beta tracks in argon, hydrogen, or nitrogen, we may infer that a free electron is not likely to enter into this kind of recombination. Electrons exchange their energy much less readily by collisions than ions do, and this difference affects all types of recombination.

As regards preferential recombination, I worked out a theory (21) fifteen years ago for Brownian motion kinetics, which is valid at high pressures, where the Langevin theory (20) applies. In the absence of an external electric field, the chance that a pair of ions created at a certain distance will escape from each other is simply the Boltzmann factor for the Coulomb energy. Even here, a strong collection field can increase the chance of escape quite appreciably: if the dielectric constant is unity, one kilovolt per centimeter gives about a ten per cent increase at room temperature. The data on recombination agree fairly well with the theory. From the variation of the current with pressure we can get some idea about the attachment distance. For air at 100 atmospheres the order of magnitude would be about 500 Å.

Certain details in the data for fields up to one kilovolt per centimeter seemed a bit puzzling at the time. I suspected that the collection field might affect the motion of the electron before attachment. This would make a difficult theoretical problem. Alternatively, I suspected multiple ionization. Now that we know more about this, it might be worth while to take another look.

Incidentally, I might have one or two suggestions, although they are hardly of the kind to decide between 10 and 100 Å, more likely to decide between 10 and 1000. One trick would be put in some scavengers deliberately. We can do that if we add some cationic soap to the water, enough to form micelles. These are probably spherical, typically of about 15 Å radius, at potentials of the order of 0.2 volts. You can load them with a great variety of dirt, such as any hydrocarbons, dyes, small particles of graphite, whatever you think the electron will stick to, and you can put in styrene. Many variations are possible. From light scattering you can determine how many micelles you have and how big they are. This is one suggestion.

About one question which came up earlier: just what effect has the dielectric relaxation? The relaxation time in water is of the order of 10^{-11} seconds. In other water-like solvents it can be varied by many orders of magnitude; in glycerol it is many microseconds. Chemically, of course, that differs a bit from water, but you might compare it with methanol. For an intermediate range, take glycol -- and you can mix the solvents. Certainly you can vary the relaxation times by many powers of ten without much change in the proportions of carbon, hydrogen, and oxygen, and you can see how that affects the results of irradiation.

LINSCHITZ: How about a comparison between the radiation chemistry of liquid and gaseous water?

MAGEE: It is an entirely different process in the gas phase. The radiation chemistry of gaseous water has been done, hasn't it?

ALLEN: A long time ago by Duane and Scheurer (22) and recently by Guenther and Holzapfel (23).

BURTON: Two years ago Dr. Onsager suggested an experiment which we are still thinking about and Dewhurst, of our laboratory, plans to do. Dr. Onsager suggested that in order to find out more about liquid water we should find out more about liquid ammonia. I don't know how the relaxation times compare, but we certainly have a different situation so far as electron trapping is concerned, in liquid ammonia as compared with liquid water. The experimental sequence would be to compare liquid ammonia and liquid water and then to compare these other things. For example, take glycerol, methanol, and glycol. Put them all, say, in water, so that you have approximately the same concentration of hydrogen, oxygen, and carbon, and then maybe you can find something here which is systematic.

GARRISON: Rollefson, of California, is working on ammonia. He has some preliminary data.

BURTON: What is he irradiating with?

GARRISON: X rays.

PLATZMAN: Measuring decomposition?

GARRISON: Yes.

KASHA: How much can you vary the relaxation time by just changing the temperature of the water at high pressure from zero to 200°C. ?

ONSAGER: You can cut it down quite a bit.

HOCHANADEL: Some work has been started by Ellison Taylor at the Oak Ridge National Laboratory on radiation effects in frozen glycerol and other glassy solvents in an attempt to learn something about the nature and number of unstable species, such as free radicals or trapped charges produced by the radiation at low temperature. A considerable study was made of the effects of radiation on solutions of methylene blue in frozen glycerol. Also, some work was done with frozen aqueous solutions of methylene blue and solutions of ferrous thiocyanate. An interesting observation concerning radiation effects in aqueous solution was that the yield of ferro thiocyanate observed on melting a solution of ferrous thiocyanate irradiated in the solid state at low temperature was greater than that for solution irradiated in the liquid state.

ONSAGER: Did he use water?

HOCHANADEL: Yes, some frozen aqueous solutions were studied.

ALLEN: I should like to come back to Dr. Kasha's question about reducing the relaxation time by heating up the water. What is the experimental effect you should look for if you irradiate the water, say, at 100° or 200° instead of 20°? What would be the experimental effect?

BOAG: With a greater relaxation time there would be a probability of the electrons becoming attached at greater distances from their parent ions. Thus, "preferential" recombination would be reduced and this change might be detectable.

ALLEN: Do you think the radicals would be formed further out because the "preferential" recombination could become less probable?

BOAG: Yes; if the electrons become attached further out, the radicals will be formed there in accordance with the view which Dr. Platzman put forward earlier.

BURTON: That is, of course, if the energy produced in the capture process is sufficient to cause dissociation of the negative ion. Electron capture does not necessarily mean dissociative capture. It is possible that, unless solvation of a product contributes to the energy requirement, the solvated electron may not survive long enough to enter into a dissociative process.

ALLEN: H_2O^- will act chemically the same as H atoms, I think.

MAGEE: It is not known that there is such a thing.

ALLEN: So you should get a bigger value of this G_R and a smaller value of

G_F. Also you would get a bigger difference between hydrogen and peroxide yields at higher temperature. However, we can argue that you affect everything else by changing the temperature, and if you did find this effect you would not know whether to attribute it to the relaxation time changes or something else. The amount of hydrogen produced would be the best index, but how to interpret this then is another matter. I plan to study the effect of increased temperatures this summer. I had not thought of going to temperatures over 100°. That would require more than one summer probably. It might be worth doing.

BURTON: The case of liquid HI may prove interesting. Dependent on the locale of capture of the electron two different chemical results might ensue. Either the electron recombines with HI^+ within the primary excitation region or gets outside and reacts with HI. In either case, no element of relaxation time enters into consideration. The alternative reactions are

$$HI^+ + e \longrightarrow H + I \qquad (a)$$

$$HI + e \text{ —— } H + I^- \qquad (b)$$

If we examine possible consequences

$$H + HI \text{ —— } H_2 + I \qquad (c)$$

$$H^+ + I^- \text{ —— } H + 2\,I \qquad (d)$$

it appears that reaction via (b) results in decomposition of 3HI molecules while reaction via (a) results in decomposition of 2HI molecules. Of course, interpretation of the results will be complicated by the contribution of primarily excited, as contrasted with ionized, states. Nevertheless, comparison of the radiation chemistry of liquid HI with that of gaseous HI (in which reaction (a) can certainly not occur in the primary excitation region) may give interesting information.

MAGEE: I think this is probably a favorable case for capture. The electron would be captured most likely as it moved away from the parent ion. In other words, I think a high percentage would form I^- before they could possibly get back. So you have many complications.

KAMEN: What dielectric constant do you associate with a protein?

PLATZMAN: The dielectric absorption at microwave frequencies has been measured (24).

POLLARD: That is one of the things that is badly needed. Practically none of the straight-forward physical constants have been measured for protein. I mean such things as specific heat, etc. I measured the thermal expansion and I found a large coefficient. It was twelve times that of copper. I was greatly surprised that no one else has done this. These measurements are certainly well worth doing.

BOAG: We have not yet decided whether the electron does get back to the parent ion or not. Today Dr. Magee has proposed a theory in which it usually gets back, but yesterday Dr. Platzman suggested that such recapture is rare. Must we leave this question unresolved for the present?

MAGEE: Possibly so. However, I do not see how it is possible to explain the chemical evidence on the basis of electrons getting away from their parent ions. It seems to me it is just completely impossible. I would not say that I have presented a calculation or can suggest any single experiment which would prove recapture, but on examining the chemical evidence I cannot think of an alternative.

BURTON: One must remember that Dr. Allen reached the same conclusion as Dr. Magee, starting in an entirely different way. That does not prove that Dr. Magee is right, but it does not prove that he is necessarily wrong.

MAGEE: Samuel and I didn't have any preconceived ideas as to how this thing was going to come out. We just wanted to put a complete model together and, as you see, there are still many loose ends. I don't want to say that any one of the things that I have presented is right. However, I didn't want to present a model for the chemical effects and conclude that the radicals are formed in very small regions without suggesting how this could happen. I gave only a sort of rough, general picture, which seems to be in agreement with a number of types of experimental observations, and I don't want you to think that I have any particular confidence in any one of the steps. The complete picture may be useful. That is my only point in presenting it.

PLATZMAN: My own view is that it is quite impossible, at the present time, to choose between the two alternatives presented by Dr. Magee and by myself. The most that we can hope for, at the moment, is perhaps a better recognition of these alternatives. I think that what Dr. Magee has done constitutes a very important advance. He has constructed the general kinetics of the chemical consequences of irradiation from some definite assumptions concerning the basic mechanism, and that is very important. But from long-time experience in chemistry we have learned to be wary about drawing conclusions as to the validity of fundamental mechanisms from the fact that their consequences seem to agree with the experimental facts. It has been proved time and time again that an incorrect mechanism can be in apparent agreement with experiment. My own approach has been at the opposite pole from that of Dr. Magee. I have started with the basic physical interactions of electron and medium and tried to find the chemical consequences to which they lead. These fundamental interactions have never before been considered properly. On the other hand, my work has not yet progressed to the stage in which the kinetics are computed. I hope that before long this may be possible. Ultimately, the final theory will very likely include a good deal from both methods of approach.

BURTON: I think this is a good time to quote O.K. Rice. He said: "The best you can say for any mechanism is that neither it nor any other that you have not thought of is necessarily incorrect."

MECHANISMS OF ENERGY DEGRADATION AND CHEMICAL CHANGE: EFFECTS OF ELECTRONIC EXCITATION

Henry Linschitz

So far in the Conference I think we have been able at least to ask a few straight-forward and more or less clearly defined questions regarding the complex problem of the fate of thermal electrons in water. I hope that the same clarity of asking questions can be maintained in this phase of the conference, because here we really go off the deep end and get to problems that are even more complex than those we have been talking about so far. Among other topics, I hope that we can get around to some matters to which Dr. Pollard has been vigorously trying to draw attention, and which are certainly relevant to the problems of radiobiology.

The problem to be discussed is the role played by electronic excitation in radiobiology. In attempting to treat the effects which ensue following the excitation of electron systems in molecules, we are confronted with all the basic problems of photochemistry plus a few further complicating factors. In the first place, the excitation is anything but monochromatic. If we regard the excitation as taking place by radiation arising from the various components of the field in the neighborhood of the rapidly moving charge, it is clear that the whole spectrum of excited states can be obtained. Since the excitation process will also involve direct impact with relatively high energy particles or recombination effects, the excited states that will be reached will be even more varied than those that can be reached by ordinary optical processes. Finally one has to take into account the role of the local distribution of excited molecules or fragments in the system. Let us list very briefly the various processes that can ensue after excitation of the electronic system or systems of the stopping medium.

First of all, of course, we can get simple fluorescence. Let me take just one moment to talk in some detail about this, because the processes encountered here must be clearly seen before trying to deal with the more complex effects. The initial excitation of a complex molecule will lead to some excited vibrational level of the upper state. For strong optical transitions, the lifetime with respect to radiation will lie usually between 10^{-8} and 10^{-9} seconds, and in any case, will not be much less than 10^{-9} seconds. States reached by particle excitation, which may have different multiplicities than the ground state, will have lifetimes much longer than 10^{-8} seconds. These radiative lifetimes are to be contrasted with times of the order of 10^{-13} seconds, which are required for typical molecular vibrations to occur. Thus, a great many vibrations may take place during the natural radiative lifetime of even the shortest-lived electronic excited states. In liquid or solid phase the vibrating molecule is always in contact with its neighbors and the vibrational energy transfer will be efficient. Hence, in condensed phase, the first process which occurs, in this simple case, is dissipation of the vibrational energy of the upper state, this energy going into local heating of the surroundings while the molecule, in the upper electronic state, falls to its lowest vibrational level. From this level fluorescence may occur after a suitable time, in general to a high vibrational level of the lower state, followed by final dissipation of the remaining vibrational energy.

Excitation may also occur into unstable states, with immediate splitting or into states which lie above the dissociation limits. If bond rupture results, the fragments A and B may themselves be electronically excited and thus carry away electronic energy, in addition to the high potential energy of the resulting free radicals.

Innumerable condensed systems are known in which excitation leads neither to photochemistry nor fluorescence, but merely to dissipation of the absorbed energy as heat. This simple observation makes it necessary to assume that there is a pathway by which the molecule can get from the upper to the lower state with neither radiation nor chemical change, and this is the well-known process of internal conversion, described by several people, Franck, Livingston, Teller, etc. (1) (2). The process is illustrated in Fig. 3.

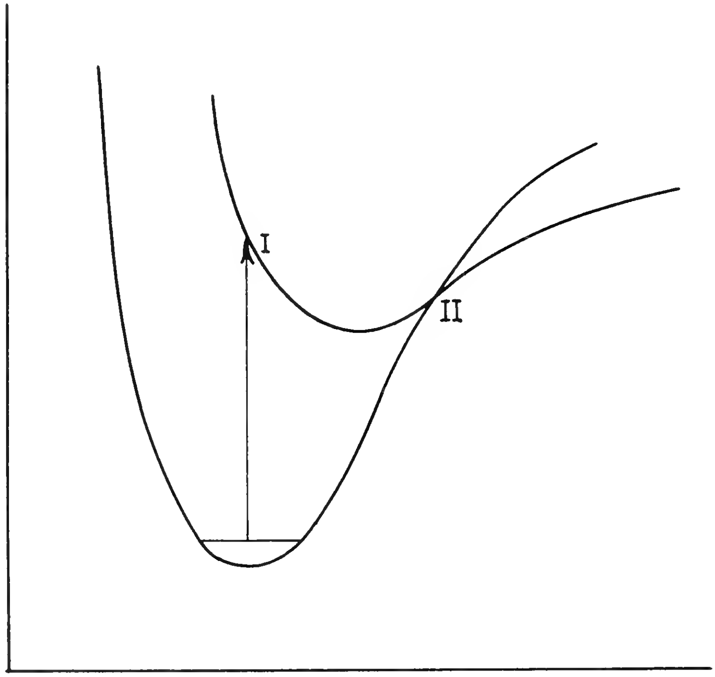


Fig. 3. Schematic Molecular Potential Curves.

Excitation raises the molecule to point I on the upper surface, from which, in its vibrations, it can reach the point II, a nuclear configuration at which one may describe the system by saying there is resonance between the upper and lower states. As the molecule swings through this configuration the electronic state may switch over from that corresponding to the upper to that for the lower curve. The molecule is thus transferred to a very high vibrational level of the lower state. In a condensed system, as we have seen, this energy is lost rapidly, and the molecule is therefore trapped in the lower state. This sequence of events is typical, and will appear again in discussions of energy migration and triplet state excitation.

Of course, it is clear that this radiationless transition may occur also to repulsive states, which is just the familiar process of predissociation.

We may now ask: What is the relative probability of heating by these various processes as opposed to radical formation or splitting? In general one can say that vibrational dissipation becomes more likely than splitting for a complex molecule - that complexity of the system alone will favor a local internal heating process rather than dissociation, for several reasons. In the first place, if we have a complex molecule to deal with there is going to be a time lag between the initial activation of the vibration and the time necessary for the energy to flow, as it surges through the various modes of the molecule, to the relevant bond that we are interested in and to rupture that bond. This time is in competition with the vibrational deactivation time which is very fast. So in general for a condensed system one might expect that if there are many modes of vibration, the chances are that the energy will pass over into local heating.

FANO: You say internal conversion can be very fast. How fast?

LINSCHITZ: Probably the best evidence comes from studies on fluoresence yields of complex molecules in solution, and it is found there that fluorescence invariably comes from the lowest of the excited electron states. The radiative lifetime for states reached by excitation in intense absorption bands, as in the case of certain dye stuffs, may be as short as 10^{-9} seconds. However, you never see any emission from the upper states in a condensed phase which would limit, let us say, the fluorescence yield to something perhaps as small as 0.01%. Any fluorescence appreciably above this would have been seen in experiments which have been done. That means that for a lifetime of the upper state of 10^{-9} seconds, the factor 10^{-4} (from the 0.01% efficiency) reduces this to the order of 10^{-13} seconds. Within this time one can say that the energy is already on its way down from the upper state, by internal conversion, to a lower state.

I would say for states like this, excitation to an upper state may lead to radiationless transition and internal conversion into a lower electronic state in a time as short as 10^{-13} seconds.

FANO: It sounds mighty fast.

LINSCHITZ: These are what the facts indicate.

PLATZMAN: Surely not quicker. You say "as short as". Well, let's not go to shorter times.

LINSCHITZ: All right. This, of course, is an extraordinarily short time - of the order of a single vibration. I do not mean that the time is always so short, but this is the limiting value and does seem to occur in many cases.

BURTON: May I say to Dr. Fano that the thing which characterizes this type of internal conversion is that it occurs in a condensed system. Thus induced internal conversion may be involved and consequently the selection rules are not so restrictive as they are, for example, for a gaseous molecule. Consequently, the internal conversion process may occur in a very short time, even as Dr. Linschitz indicates, in a single vibration period.

KASHA: It is not much longer than a vibration period; that has been proven quantitatively.

BURTON: Internal conversion may be the precursor either of decomposition or of a simple energy degradation, for example by fluorescence. If decomposition occurs, the total process is called predissocitaion. Such predissociation processes, require anything from 10^{-13} seconds up. A similar statement applies, of course, to internal conversion. The time requirement depends on the necessary process and the probability of that process. There are two kinds of internal conversion: induced and the spontaneous. Induced internal conversion is more probable in a condensed system than in a gaseous system.

FANO: Wouldn't it perhaps be possible to say that what this 10^{-13} seconds really represents is the time required for the atoms to get out of the position from which they can drop down, so that direct fluorescence will be forbidden by the Franck-Condon principle, but it does not imply there has been within the 10^{-13} seconds anything like substantial transfer of energy to vibration?

LINSCHITZ: I would agree with that. Certainly several vibrations are necessary before appreciable energy can be bled away from the molecule by collisions. However, you only need one vibration period to excite the full amplitudes in a particular mode.

The question was asked how rapidly these processes occur. Of course, once a moleculesis in an excited state possible processes may occur which will stop the fluorescence. Conversion into a metastable tautomeric state, which has never been clearly shown to exist, would also make this a short lifetime but even conversion to a tautomer requires that the molecule be trapped with loss of vibration energy, somewhere, in order to have any effect on the fluorescence. That trapping process essentially consists of the loss of a certain amount of vibration in the condensed phase, since this is the only thing that makes the tautomer metastables. So that if you are talking about processes that will lead to heating, these may occur in very short times -- processes that will lead to heating subsequent to excitation.

FANO: To some heating.

LINSCHITZ: To some heating, that is right. No matter how far down you drop.

KASHA: It might be only half a volt in general. Only a small fraction of the electronic energy is degraded in any single internal conversion among other states.

BURTON: Do you say the electronic energy is degraded during the internal conversion process or subsequent to it?

KASHA: Well, you start with 6 volts of pure electronic energy and you convert it to 5 volts of electronic energy. Incidentally, I disagree with Dr. Burton about one thing. In diatomic molecules what he says is certainly true, but I think the real point of Dr. Linschitz's talk is that for the polyatomic molecule the time of conversion is not even 10^{-9} seconds. It has to be closer to 10^{-12} or 10^{-13} because otherwise you would observe emission from these upper states.

BURTON: Is this a liquid you are talking about?

KASHA: In liquid or vapor at moderate pressures.

BURTON: I think there is evidence to the contrary. For example, in the aldehydes these internal conversion processes occur, and they occur slowly.

KASHA: How does one know that? You see, all the absorption bands in the excited states of these molecules are diffuse. That is a novel feature compared with diatomic molecules.

BURTON: Perhaps we are going too far afield. We can save this point for private discussion.

LINSCHITZ: This is certainly a lower limit for the time that we could get in general. Possibly if you want to say that the fluorescence measurements would pick up even as much as 0.1 per cent, then 10^{-12} seconds, which would allow several vibrations to occur, would be the time required for internal conversion. These times, though, are by no means well defined and of course are sensitive to the nature of the vibrational modes that are initially excited.

We were discussing the factors that would channel the original electronic excitation energy either into vibrational dissipation or bond rupture. In particular, the role of molecular complexity favors the former because of the long time required for bond rupture. For complex molecules there is also a better chance for matching the vibrational levels of one electronic state to those of the next lowest state. So that this would also be a factor that would make it easier for a complex molecule to lose energy by this process than for a simple one in condensed phase.

Finally I want to point out that for complex molecules, especially those with large aromatic systems, the lower electronic states are more likely to be stable than are those of simple molecules, so that for this type of case you can expect to get possibly a couple of electron volts of energy set free when the molecule ultimately ends in the lowest excited electronic state even if fluorescence can occur. For a complex molecule the very fact that there are so many excited states which may be stable would also tend to concentrate heating effects at those sites, since the tendency may be to release vibrational energy in relatively small amounts.

KAMEN: What you are saying is that any biological molecule you can think of is already so complex that the chance of getting --

LINSCHITZ: I would not go so far as to say that categorically. You have these two competing processes and in general you are going to get less free atom formation with the more complex molecules, but it can be shown that if you take molecules even as complex as aniline, excitation in the ring will lead in the gas phase to splits of the C-N bond which can be prevented by the admixture of simple gases into the system.

KAMEN: How do you account for the localization of energy in one bond in this picture?

LINSCHITZ: This is a function entirely of the shape of the energy surface, of the mode of vibration which happens to be excited in transition and of the time required for collisional deactivation. Again one has no knowledge at all for this complex system of how the energy surface lies, and I would hesitate to try to make any systematic rules. However, if the chromophoric group is adjacent to a vulnerable bond, internal conversion may lead to rupture in that nearby bond before the energy has had a chance to get diffused through the various modes. This is the case in aniline and other complex molecules.

BURTON: Would you mind stating which bond it is that breaks?

LINSCHITZ: The bond between the carbon and nitrogen. Hydrazine is formed. This is some work of Terenin et al (3) about 1939.

KASHA: May I make one point about heating. It is possible that local heating does not always accompany these processes. For example, what about infrared (IR) emission?

LINSCHITZ: This is a very slow process. What would you estimate to be the time for IR emission?

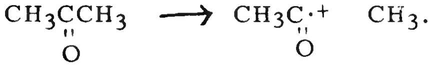
KASHA: I do not have any oscillator strength data for a single IR vibrational band. However, if quenching collisions are successively decreased in rate, as for example, at low temperature, certainly IR emission of vibrational energy may become important.

MAZIA: Does internal conversion imply the absence of chemical change in the usual sense?

LINSCHITZ: This is competition for the chemical change. That is, the very rapid loss of energy as heat here will tend to compete with free radical formation.

BURTON: May I ask another question. Do you remember the quantum yield for the photolysis of aniline?

LINSCHITZ: No quantum yield is given in the article by Terenin. In consequence of this kind of radiationless transition from one level to a lower one, we might expect to find a shift in the energy from the region in which the excitation originally takes place to the bond which is ultimately ruptured. For example, one of the few pieces of photochemistry on fairly complex molecules that seems to be well established is the case of certain ketones, in which excitation of electrons that are undoubtedly in the carbonyl group leads to bond rupture in the less strong adjacent C-C bonds. Thus in acetone, we have:



$$CH_3\underset{\overset{\|}{O}}{C}CH_3 \longrightarrow CH_3\underset{\overset{\|}{O}}{C}\cdot + \quad CH_3\cdot$$

However, we would not expect this vibrational energy to move very far through the molecule before being degraded in liquid systems.

With regard to even more complex molecules, I might mention some photochemical studies on stearic acid anilid monolayers on water, which are relevant here (4). Excitation in the aromatic ring leads to hydrolysis of the relatively weak amide link with quantum yield of about 0.2. So that in general although one might say that the tendency here is to lose vibration in a general process of degradation, this vibrational loss is very closely coupled to adjacent bonds, as we might expect in some cases.

KAMEN: This is a gas reaction?

LINSCHITZ: This is in a monolayer.

KAMEN: Are there any data on the effect of X rays?

LINSCHITZ: I don't think so. I have never seen any paper on it.

BURTON: Do you mean for this case or a comparable one? Dr. Linschitz knows about the work that we did on the benzene system.

LINSCHITZ: Yes, I want to come to that.

CURTIS: May I ask how you know you produce the excitation of this one bond?

LINSCHITZ: Simply by the absorption spectrum and the wavelength of the exciting light. It is known that the excitation appears originally in the aromatic part of the complex molecule. I might say that the various possible, almost circumstantial, shapes of energy curves which happen to be involved in the transition -- just those special modes of vibration that happen to be involved will result in subsequent photochemistry or lack of photochemistry because this will set up specific preferred channels for the vibrational energy to follow through the molecule, after internal conversion. As a general rule, one can say that the more complex the system the more will be the tendency to heat up rather than to split, but if there are weak bonds adjacent to the chromophore these may break also.

To go on to the bimolecular processes which might be involved, I think the most important one from the standpoint of radiobiology is oxidation or reduction of the excited molecule.

In the simplest case, an excited molecule MH_2^* can lose a hydrogen atom (or electron) to a suitable acceptor A to form a pair of radicals:

$$MH_2^* + A \longrightarrow MH\cdot + AH\cdot$$

If A is oxygen, this leads to the powerful oxidizing radical HO_2. Several reactions may now ensue. The two radicals may react further to give $M + AH_2$, or $MH\cdot$ can react with another molecule RH_2:

$$MH\cdot + RH_2 \longrightarrow MH_2 + RH\cdot$$

regenerating MH_2 and permitting

$$RH\cdot + AH\cdot \longrightarrow R + AH_2.$$

In this case MH_2 acts as a redox catalyst. This is probably the simplest mechanism one can write for photo-sensitization by MH_2.

BURTON: Give us an example of that, please.

LINSCHITZ: The photo oxidation of amines by oxygen, sensitized by chlorophyll (5) essentially runs through such a sequence.

Another possibility is for MH_2^* to react as an acceptor rather than donor, to give again a pair of radicals

$$MH_2^* + RH_2 \longrightarrow MH_3\cdot + RH\cdot$$

and subsequent reactions analogous to these given previously.

As evidence for this, one can cite experiments on fluorescence quenching of various dyes by oxidants or reductants and the observed over-all photochemical effect, sensitized oxidation-reduction (6).

Which of these various processes can occur depends ultimately of course on the redox potentials of the various excited molecules and substrates, the rates and just what happens to be in the neighborhood.

Most of the available data on the various bimolecular processes represented here come from experiments on very complex molecules, mainly dyes with low-lying energy levels and with relatively stable semiquinones. There is certainly a need for photochemical studies of molecules of intermediate complexity and bio-chemical relevance, to ascertain which of the various processes may occur (7).

The main point to make is that these bimolecular processes afford a mechanism whereby one can obtain active radicals without the expenditure of the energy necessary to ionize water and either allow the ions to recombine or to split water into radicals by the various processes that have been discussed by Dr. Platzman and Dr. Magee. This is an economical way in general of reaching such activated intermediates, and in particular HO_2.

KAMEN: Isn't there some difficulty about distinguishing between a direct hydrogen transfer this way and the intermediate ionization of water? If water is in the vicinity how do you tell if you have, for instance, a transfer of electrons through a chain of intermediates like this or one where you simply ionize water first and then produce the water radicals? There is no way of distinguishing it, is there? Give us an example. How do you tell which reaction is going on in the system?

LINSCHITZ: If a model reaction can be shown to go with visible or ultraviolet radiation, at least the possibility of its taking place directly under high-energy radiation is demonstrated. To be entirely sure however, we would have to know the actual yield of electronic excitation relative to water ionization. This is a problem which I don't want to speak on at all. I had hoped that by this time we could have some idea as to what the fraction would be.

FANO: Aren't these the mechanisms that are quite effective when you have photochemistry with ultraviolet light because the ultraviolet light can be made use of only by these systems, but when you throw in ionizing radiation, the fraction of ionizing radiation that would go into that would be very small because there are few groups that can do this.

LINSCHITZ: This problem will appear again and again in this whole session. It seems to me that what you have to contend with here is first of all the total amount of excitation that will be picked up by these molecules and, second, how strategic these molecules may be in the subsequent radiobiological effect. Granted, most of the cell is water but if energy is transferred specifically into a single site, say on a nucleic acid chain, it may possibly, erg for erg, be more effective there.

BURTON: Do you mean that when you use ionizing radiation you can produce a great diversity of excitations only one of which, say, can contribute to the phenomenon that you are talking about? Is that what you are saying?

FANO: No. What I was saying was that the number of groups that can do this is comparatively small percentwise; therefore, only a small fraction of the radiation energy goes into them.

BURTON: However, most of the internal conversion processes may lead to a single state which results in the radiobiological effect. I don't mean to say that the energy will be as efficiently used because, after all, there will be a larger amount of energy dissipated thermally in a case like that. However, it may very well be true that a very large fraction of the excited molecules ends up this way. That is quite different from the suggestion of uniformly very high energy efficiency. That is correct, isn't it, Dr. Linschitz?

LINSCHITZ: Yes. I want to talk later about the process of energy transfer. The main point I want to make at this stage is this: Here is a way in which one can introduce radicals possibly in strategic places in the protein or nucleic acid part of the cell without the expenditure of as much energy as is necessary to form these radicals by ionization and subsequent processes.

While I am on this point I might mention another possible way of getting radicals cheaply into the cell. That involves the excitation of heavy metal complexes which exist in the cell, again in relatively small concentration but yet again possibly in vital places in the cell. Many heavy metal complexes exist which have intense absorption hands comparable to those of dyes (8). In some cases, these bands may even lie in the visible. Excitation of these complexes certainly involves electron transfers within the complex which may again lead to free radicals with relatively low energy expenditure. Thus, a typical case would be (9):

$$(\mathrm{Fe}^{+++}\,\mathrm{OH}^-)^{+++}\quad(\mathrm{Fe}^{++}\ \mathrm{OH})^{++}\longrightarrow\mathrm{Fe}^{++}\ +\ \mathrm{OH}\cdot$$

On this whole matter of the energy which is necessary to introduce radicals into the system, I should like to show some evidence that this energy may really be very small even for molecules of not too high a degree of complexity. This is based on work of G.N. Lewis and his group in which direct photo-oxidation processes were studied.

Lewis and Lipkin (10) were able to demonstrate the formation of known semiquinones or radical-ions of certain organic molecules (aromatic amines, phenols, dyes, etc.) when these substances were illuminated in glassy solvents at low temperatures. Thus, they postulated that processes of the following type occurred:

$$\mathrm{RH}\ \xrightarrow{h\nu}\ \mathrm{RH}\cdot^{+}\ +\ e,$$

which might be followed by

$$\mathrm{RH}\cdot^{+}\ \longrightarrow\ \mathrm{R}\cdot\ +\ \mathrm{H}^{+},$$

since the spectra of $\mathrm{RH}^{\cdot}$ or $\mathrm{R}^{\cdot}$ were found in the glass after illumination. By using suitable solvents (containing amines of low molecular weight) we have been able recently to demonstrate the existence in the illuminated glass not only of the absorption bands of the organic radical but of the solvated electron as well (11). In the solvents we used (mixtures of iso-pentane, triethylamine and methylamine) the solvated electron absorption appears as a broad band starting at about 7000 Å and extending into the infrared at least as far as 14,000 Å. There is thus no doubt that the photo-ionization (or photo-oxidation) process suggested by Lewis and Lipkin does occur in organic solvents.

When the rigid solvent is softened by warming slightly, the absorption bands of organic radical and electron both disappear together, and the spectrum of the original organic molecule is restored quantitatively. This recombination process is frequently accompanied by light emission and we have established that this luminescence is identical with the normal phosphorescence of the original molecule, which may also be observed in rigid solvents. Since this phosphorescence is known to arise from triplet states of the molecule, we thus have direct evidence of the formation of such triplets by electron-radical recombination tion. We will return to this matter later. The main point that I want to make at this time is that surprisingly low excitation energies may result in photoionization or photo-oxidation of these organic molecules in solution. For many aromatic molecules with reasonably stable semiquinones (i. e., those which are stable in rigid solvents at liquid nitrogen temperatures), radicals or radical-ions are formed by excitation in the middle ultraviolet. A knowledge of these threshold energies is of course necessary for evaluating possible mechanisms of radiation action. Photochemical studies in rigid solvents, of the type just described, combined with data on relative oxidation-reduction potentials, should help establish the ionization energies of a variety of organic molecules in solution.

KASHA: May I make a comment? Glasses or mixtures of organic liquids which when supercooled at a liquid nitrogen temperature form a homogeneous glass have been used for quite a long time in spectroscopic work. Lewis and Lipkin were the first to develop glasses which did not crack at low temperature, and they in general used ternary systems, the more common of which was ether-isopentane-ethanol. They also substituted ethylamine for the alcohol.

LINSCHITZ: In these mechanisms discussed so far, the transfer of energy takes place by the formation of high-energy fragments (either by unimolecular or bimolecular processes) followed by further reaction of these fragments. I should like to move along now to processes involving several molecules - in particular, resonative energy transfer. This kind of "broadcasting" process has been known for a long time, going back to the work of Franck, Cario and others on sensitized fluorescence. Kallmann and London calculated long ago that, in the case of completely sharp resonance, for instance between an excited and normal sodium atom, cross sections for energy transfer could be obtained of the order of 1000 times the ordinary gas-kinetic cross section. More recently attention has been drawn to this process by the work of Kallmann and his group on scintillation counters (12). It is found that certain organic hydrocarbon crystals emit light under ionizing radiation. If the crystal is melted, the luminescence is immediately quenched. But the addition now to the liquid solvent of small amounts of fluorescent substances, in particular those having absorption bands lying to the red of the original solvent absorption, again restores the luminescence in high yield. In this case, practically all of the radiation is absorbed by the solvent and the problem is to find how much is transferred to the solute.

Kallmann has measured energy yields for light production in alpha or gamma irradiated anthracene crystals. His value is certainly correct to ± 50%, which is all we need for our order-of-magnitude argument, and he finds that the energy efficiency for the conversion of gamma energy into light is about 10%.

That was for anthracene crystals, for which the fluorescence yield (ultraviolet light) is nearly 100%.

For solutions of anthracene in xylene, the optimum concentration for gamma-light conversion is about 1 molecule of anthracene per 1000 of xylene. At this concentration, the (ultraviolet excited) fluorescence yield is about 20%. If all the energy were transferred from xylene to anthracene, we would therefore expect to obtain an energy efficiency of 20% that of the crystal, or 2% over-all. Actually, the observed yield is 1%. So these figures mean that you are getting roughly 50% of the energy transferred out of the xylene into the anthracene.

ALLEN: Do you consider the difference between 1 per cent and 2 per cent is outside the range of error?

LINSCHITZ: Probably not, but the important thing is the order of magnitude. The fraction of energy which is transferred from xylene to anthracene could be 100% or maybe 10%, but is certainly very high, because you are always dealing with a solute-solvent ratio of 1:1000.

The mechanism of this transfer presumably is the same as that in sensitized fluorescence, except that in these systems vibrational deactivation operates to trap the energy in the molecule whose absorption lies furthest to the red (13). Suppose we assume that a molecule of solvent is excited into some arbitrary state. Any excess vibrational energy will be lost quickly. If another molecule is now adjacent, energy transfer may occur to that vibrational level of the second molecule which offers the best energy match or resonance with the first. Any excess vibrational energy of the second molecule will then also be quickly dissipated, so that the resonance is destroyed and the energy cannot get back to the original or similar molecule. In this way the energy may drift to molecules having still lower lying excited states, as demonstrated by Kallmann, until ultimately, fluorescence or radiationless transition to the ground state occurs.

CURTIS: Did I understand you to say that the maximum energy efficiency is 50% when the ratio is 1 to 1000?

LINSCHITZ: That is correct.

CURTIS: If this picture is correct, why would it be a maximum?

LINSCHITZ: Well, it turns out that if you plot the fluorescence efficiency of anthracene, for example, as a function of its concentration, then you find a curve with a maximum. A phenomenon called self-quenching appears, so that as you go to higher anthracene concentration, although you expedite the resonative transfer from xylene to anthracene, you run into the self-quenching effect and that cuts down the total light yield. This ratio, which is roughly 1:1000, represents the optimum product of the probability of energy transfer into the anthracene and the lack of the quenching of the anthracene by itself.

FANO: Quenching means that the light is emitted but it is captured again by some other anthracene and it does not get out?

LINSCHITZ: No, this is not quenching due to absorption of fluorescent light.

FANO: What sort of quenching is this?

LINSCHITZ: The actual mechanism of self-quenching is really a problem. Of the many theories probably the one which makes the most sense is that of Förster (6). Coupling between two dipolar oscillators leads to two states, one symmetrical and one anti-symmetrical, of which the anti-symmetric will be the state of lowest energy and longest radiative lifetime. The increase in the radiative lifetime due to this coupling then permits more of the excited molecules to lose their energy by competing radiationless processes. This is one possible mechanism of self-quenching.

KAMEN: Does Pringsheim have anything to say about this?

LINSCHITZ: I think Pringsheim's book (14) appeared too early for this theory to be included. But the shape of the quenching curves and concentrations agree pretty well with Förster's quenching theory. I don't want to get into this problem as such unless it is interesting. I want to talk in some more detail about the process of resonative energy transfer, which Förster treats also in detail. Kallmann's experiments show that the probability of such energy transfer is so great that the energy may go through a thousand xylene molecules to reach an anthracene before it is lost by thermal quenching in the xylene. This is itself so strong that no xylene fluorescence can be observed in the pure solvent. The actual times necessary for the transfer are really uncertain. I wish I had some better estimates than the ones I want to give, but the data just are not at hand. At any rate, one can make rough estimates of the jumping frequency of the energy by saying that this frequency would be very roughly the resonance energy arising from the coupling of two oscillators, divided by "h". If we take the resonance energy to be even as small as 0.01 of a volt, then the frequency comes out to be 10^{12} jumps per second.

ALLEN: How do you define this resonance energy?

LINSCHITZ: This is just the energy of interaction of two dipoles at distance R. The resonance energy will go as the product of the dipole moments times a function involving the angle between the dipoles divided by R^6. The point here to be noted is that this energy is extremely sensitive to the separation of the molecules. The dipole moments involved here are the total transition moments obtained from integrated absorption of the molecule. You get R values of the order of 50 to 60 Å, corresponding to, say, 50% transfer probability in 10^{-8} seconds.

KASHA: How does the collision frequency compare with the time for energy transfer from the primary excited molecule?

LINSCHITZ: Do you mean for these distances?

KASHA: You calculated a time from the resonance frequency as you put it.

LINSCHITZ: 10^{-12} seconds for interaction energy of 0.01 volt.

KASHA: That has to compete with collisions between solvent molecules, doesn't it?

LINSCHITZ: It has to compete with quenching of the energy in the solvent molecule, that is true. The probability of this isn't known actually because of the unknown increased lifetime for radiation in the solvent molecule due to the coupling effect I spoke of in answer to Dr. Fano's question. Since you have no way of knowing what the true radiative lifetime is in the solvent, the absence of solvent luminescence doesn't tell you very much about the quenching probability. The way you can estimate the net lifetime in the solvent alone is to measure the yield of the competing process of energy transfer into the solute, and then estimate the inherent probability of this latter transfer.

KASHA: It may be a minor point, but the idea is then if you have liquid benzene all by itself and you excite it with the light which benzene is capable of absorbing you say that no light is observed as emission because the lifetime is too long. How long do you have to wait for that result?

LINSCHITZ: What you are trying to explain is the existence of the effect of self-quenching. This can be explained by assuming that the coupling of the emitting molecules with each other increases the radiative lifetime, so that even improbable quenching transitions can be effective. In the pure solvent you have the self-quenching to a very high degree, and for that reason it is hard to say just what the "inherent time" for radiative transition or quenching transitions means.

POLLARD: Are those pretty big dipoles which are effect at 50 and 60 Å?

LINSCHITZ: Yes, these are very strong. The 60 Å value is actually obtained from experiments, and calculations on dye solutions. The mechanism for energy migration may involve molecule to molecule jumps, but there is also a possibility that it may move a great distance in a single jump.

At any rate, in liquid scintillation counters, I think the relevant point to make is that energy can migrate through at least 1000 molecules in times of the order of 10^{-9} seconds or possibly smaller.

KAMEN: Is this the mechanism that is used for the transfer of energy in the chlorophyll case?

LINSCHITZ: Probably so.

POLLARD: It is phrased a little differently by Arnold and Oppenheimer (15), but it amounts to this: it is a dipole-dipole interaction.

KASHA: In the chlorophyll system you never do the experiments under the same conditions. You never have a homogeneous solution and you never can tell whether co-adsorption is required or not.

LINSCHITZ: Energy migration is, of course, very intriguing from the standpoint of biochemistry, and I should like to point out that certain cell systems seem uniquely well fitted for such transfer. Evidence, which is, of course, still very incomplete, indicates that the DNA molecule is a kind of long thread with the aromatic bases oriented parallel to each other along the thread, and furthermore that the distance between the purines and pyrimidines is extremely small, of the order of 3.5 Å. At such small distances one can certainly expect that these aromatic rings will be very strongly coupled to each other. If you assume, say, 3000 such rings, roughly, for a molecular weight of 1 million for a DNA molecule, this is within the range for which energy can be transferred through the whole DNA chain from a single activating step.

KAMEN: Is there any recipe for specifying the kind of a system in which you expect this to happen?

LINSCHITZ: The systems that favor this most are those with intense transitions, which overlap each other in fluorescence and absorption bands, and speaking generally, which have absorptions which lie as far out to the red as possible.

KAMEN: In other words, almost any peptide?

LINSCHITZ: Essentially anything biological except water.

ALLEN: With scintillation counters do you always use aromatic materials?

LINSCHITZ: You can use a hexane solvent or dioxane, with an efficiency of about half what you get with aromatic materials.

FANO: While it is true that anything biological has aromatic rings, still the percentage of electrons in aromatic rings among the electrons of a biological material is small.

The whole biological process is designed to make use of the low grade excitation of a prosthetic group, whereas ionizing radiations produce high grade excitations of all groups indiscriminately.

LINSCHITZ: Let's come back to that objection for discussion later, because it's obviously important. For the time being, assume that we have an electronically excited residue on a DNA chain. Then, if one has anywhere along the chain a molecule with absorption bands which lie somewhat to the red of those for the majority of molecules in the system, then one can expect by the trapping mechanism shown previously that the energy will funnel into this site where it will either give rise to fluorescence, intense local heating, or any of the radical formation processes we spoke of earlier. I think that any of the arguments which deal with the biological effects of radiation will have to take account of these simple, and I think fairly reasonable physical, processes.

KAMEN: May I ask one question that has bothered me for about two or three years. That is, the significance of cavitation in supersonic radiation. According to all your notions you have to have enough energy to get at least a few vibrational levels above the ground state. The amount of energy involved in supersonic radiation is not enough for that; yet you get enormous biological effects out of these things.

POLLARD: They seem to be frictional effects. In studying a bunch of viruses, the effect certainly goes with size. The bigger the virus, the more the chance for damage. In other words, the more the structure, the greater the chance for damage.

PATT: Did Dr. Linschitz say a single activating event could involve 3,000 DNA molecules?

LINSCHITZ: No, 3,000 purine or pyrimidine rings. The same thing might occur in proteins, of course, in which energy transfers can take place between aromatic centers within the protein molecule. Photochemistry of the proteins indicating that this does occur in some cases. For example, Franck and Livingston (16) have discussed the case of the photochemical splitting of the CO-myoglobin complex, with light absorbed by the protein part of the molecule. Presumably, this energy must be transferred to the porphyrin to cause dissociation. Using Förster's theory and the known concentration of porphyrin in the system, one can estimate crudely the time required for energy transfer from protein to porphyrin. This turned out to be of the order of 10^{-12} seconds, which is within the possible lifetime of the electronic energy in that molecule. In this case it appears that such energy migration is quite likely.

POLLARD: Should there be any thermal influence on this? If you cool a molecule down should you get more or less transfer?

LINSCHITZ: I imagine that you probably get less effect because as you cool down you sharpen the fluorescence and absorption bands and thus diminish the overlap. On the other hand, if you warm the thing up you can enhance the probability of vibrational quenching, in which case less energy is available for transfer. What you would get would be a balance of these two factors.

POLLARD: So you should have a maximum?

LINSCHITZ: There should be some maximum, yes.

POLLARD: It has not been observed. For example, it has been observed, in the inactivation of catalase by ultraviolet, that it goes very definitely down at low temperatures to a minimum which is not zero and rises sharply at high temperatures.

LINSCHITZ: What is the quantum yield?

POLLARD: One, or something in that magnitude.

LINSCHITZ: I have just one more point to make in this matter of what can be learned from scintillation counters regarding biochemical effects, and that is the change in the efficiency of the scintillation counters as one goes from gamma to alpha irradiation. It is found, again by Kallmann, that alpha irradiation gives an efficiency of light conversion of about 10 percent of the gamma energy. It is difficult to say just what the mechanism is of such enhanced quenching in the alpha case.

BURTON: Yesterday I was told that for sodium iodide the efficiency is approximately the same for gamma and alpha.

FANO: For ionorganic materials it is. For the organic it isn't.

ALLEN: There is a theory on this by J. B. Birks (17). The idea is that along the track of the alpha rays many damaged molecules are produced which are capable of quenching the excitation. They are apparently formed in a shorter time than is required for the excitation to get this far, and since there is a high concentration of them, the light emission is quenched.

BURTON: These molecules happen to be the kind that are not very badly damaged by radiation; that is, the $\underline{G}$ value for the decomposition is very low.

PLATZMAN: I agree -- and for this, and certain other reasons, I have been skeptical of their part of Birks' theory.

KASHA: There is one other difference here which I am reminded of from a conversation with Dr. Boag. That is the difference in the Cerenkov radiation. If it were active in being absorbed in the vacuum ultraviolet range, it would give quite a difference. It would, in fact, make gamma radiation more efficient, as you say it tends to be.

LINSCHITZ: A factor of ten?

ALLEN: The intensity of the Cerenkov radiation is known to be relatively low.

LINSCHITZ: I have only one more point to cover. That is the possible role of triplet states in all of this. Ideally, if we want to get a complete theory for the function of electronic energy in radiobiology, we should like to know such things as the actual energies which are excited, the yields of each level and the lifetime of each level. The latter is especially relevent.

Some years ago triplet states, especially of complex aromatic or unsaturated molecules, came into prominence through the work of G. N. Lewis and his group on the spectroscopy of organic molecules in rigid solvents. The rigid medium impedes radiationless quenching to the ground state and thus stabilizes the molecule long enough to see the long-lived triplet excited states in phosphorescence, or even in absorption. For these triplets radiative lifetimes lie in the range of possibly 10^{-4} to one second, which are very long lifetimes, indeed. In addition, these molecules are interesting chemically because they are diradicals. Thus ethylene in the triplet state would be written by a chemist with two unpaired electrons, available for bond formation. These two properties make such states very interesting as possible intermediates in the photo-chemical processes that can occur.

Another feature of the triplet state is that although it is reached generally with low efficiency optically, it may be excited with high efficiency by ionizing radiation, in particular, via recombination of ions and electrons. This was seen, for example, in the rigid solvent experiments cited earlier, in which the recombination luminescence corresponded to the triplet-singlet emission. Optically, the transition will occur between the singlet ground state and other excited singlets, and the probability of getting into the triplet state is relatively small because of the restriction on the radiationless transition between the singlet and triplet.

KASHA: Could you state that again, please, because I don't think it sounded right.

LINSCHITZ: The probability for getting into the triplet state from the excited singlet is relatively small.

KASHA: You mean from the ground state?

LINSCHITZ: From the excited singlet. I mean optically getting into the excited singlet followed by radiationless transition into the triplet.

KASHA: If you have not seen the paper by Gilmore, McClure and Gibson (18), they have shown that at least for the half dozen cases they studied the quantum efficiency of the triplet-singlet emission is close to unity for several molecules none of which contain any heavy atoms which would enhance spin-orbit coupling.

In other words, the probability in many complex molecules of going from the singlet to the triplet is very high.

LINSCHITZ: Are not these molecules studied in rigid glasses in which the deactivation of the excited singlet is relatively slow and the competing triplet conversion from that state can then occur with high yield? If you take, on the other hand, the average aromatic molecule in a liquid solvent I wonder what would be the yield.

KASHA: The yield is zero, but you cannot say that it does not get into the triplet state just because you cannot see any emission.

LINSCHITZ: That is true.

KASHA: In fact, that has been demonstrated by others.

LINSCHITZ: Has anybody measured triplet yield in cases where you do not have such short lifetimes for the excited states?

KASHA: Those were the ones covered partially by McClure, Gilmore and Gibson. The singlet-singlet probably would give a lifetime of about 10^{-8} sec -

onds.

LINSCHITZ: From the absorption spectrum?

KASHA: Yes.

LINSCHITZ: I see. These figures are very relevant. What kind of molecules were they?

KASHA: Among them were aromatic ketones which are electronically peculiar in a certain sense and that really is why they do this.

I think there is one missing link in what Dr. Linschitz presented, and this has to do with what is the longest time an internal conversion takes. If it is 10^{-13} for a singlet-singlet radiationless transition, and there is a prohibition factor as great as 1 million for an inter-combination at the same time that an internal conversion takes place (in other words, an internal conversion between a singlet and triplet state) then you multiply the latter by 10^{-13} and you still get 10^{-7}. If the singlet-singlet fluorescence lifetime is comparable, then, so that 10^{-7} can compete with it very well, then between those processes there is about equal competition (19). There is really bi-partition of the electronic energy, but in some molecules that takes place overwhelmingly in favor of intercombination, so that triplet-singlet emission is the main one observed and that includes aromatic ketones, aromatic nitro compounds and aromatic N-heterocyclics, which are not only fluorescent but they are also phosphorescent if observed in any rigid system.

LINSCHITZ: In any case there is another process by which one can get to the triplet state, with certainly indisputably high yield, and that is recombination of the radical ions, R^+, and electrons that have been set free. You would excite the triplet state with a yield of 75 per cent for this process.

FANO: When you have ionizing radiations all the slow secondaries can give you a singlet-triplet transition easily.

BURTON: I want to ask just one question that I want to be clear about. When you say a singlet-triplet transition is an internal conversion process do you mean to rule out the possibility of these processes occurring between two molecules? As you know, if two molecules are involved, the multiplicity selection rule may be much less restrictive.

KASHA: It could work except there is one thing that rules against it. Don't you think that those experiments of McClure (20), and of Yuster and Weissman (21), in which they substituted heavy atoms right in the same molecule, showed that the transition possibilities were influenced within the single molecule?

BURTON: I was not arguing. I just wanted to ask the question.

KASHA: I think that might rule it out.

LINSCHITZ: I don't know if everybody is acquainted with those experiments Dr. Kasha mentioned. What was done was to substitute progressively into a given molecule various heavy atom constituents which would enhance the spin-orbit coupling. It was found by Weissman and Yuster, and by Dr. Kasha that the yield of phosphorescence increased along with the atomic number of the substituent, and the lifetime of phosphorescence decreased, indicating that what you were dealing with was transition involving a change in multiplicity within a single molecule. At any rate, certainly by recombination of the radicals and electrons as well as by direct electron excitation one should obtain a good yield of triplet states.

The observation has been made by the Notre Dame group that aromatic molecules tend to protect aliphatic molecules with respect to radiation decomposition. I once pointed out that this type of process may be explained by triplet state formation. If irradiation leads to an aliphatic radical ion, A^+, then charge transfer may occur to the aromatic molecule B, in the system, giving $A + B^+$. The B^+ ion would then combine with the electron to give stable excited states, triplet, or singlet. If recombination occurred between the aliphatic A^+ and the electron, repulsive states would occur and bond rupture result.

BURTON: At the present time I may say that I no longer advocate that particular mechanism. I think it is more likely to be an excited molecule mechanism rather than an ionic one.

LINSCHITZ: In any case even if energy rather than charge is transferred, this would give you a triplet molecule which in the aromatic case is stable whereas in the aliphatic case it is unstable. This conversion will bleed the energy off as heat.

That essentially covers what I wanted to say.

FANO: I would like to elaborate a little on a point I made earlier. It has come out from subsequent discussion with Dr. Linschitz that the question he had in the back of his mind was what fraction of the energy delivered by ionizing radiation goes into excitation, and now the question is, what is meant by excitation. Let's try to distinguish just roughly between energy transfers to molecules above and below something like 12 to 15 electron volts. Whatever is above is probably what I would naively call ionization and below 12 to 15 volts would be what I would naively call an excitation. But probably excitation in the meaning of Dr. Linschitz and of photochemists in general is really something considerably lower, say below 5 volts which is the sort of thing which is known to be taken up by the chromophoric group in photochemical reaction. So maybe one could ask first how much is below the 5 volt limit, how much is above the 12-15 volt limit, and how much is in between. I would say the primary criterion for trying to answer a question like this is what portion of the total oscillator strength lies in these different ranges, and I would say I don't have any information, but I would be inclined to say that probably the ratio of above to below the 12-15 limit for any sort of ordinary material is of the order of half and half. I am just taking it from hydrogen, but that must be quite general.

Incidentally, this fraction depends on the ionization limit in a queer manner. The higher the limit the more probable it is that the energy absorption goes above it. It is just contrary to what one might expect.

When it comes to saying how much of the energy goes below the 5-volt limit, then I would say that this is probably a very small fraction. It is a small fraction for the reason that the percentage of electrons in the material which can absorb such low amounts is small. If many of the electrons in organic matter were ring electrons of aromatic molecules, then the great majority of the energy will go below 5 volts. But the percentage of electrons in the material which belong in aromatic rings or any how to double bonds is extremely small. I haven't made any calculations and I don't know, but I would say probably a few per cent.

POLLARD: Have you looked at the measurements of Ruthemann and Lang (22)?

FANO: No.

POLLARD: They are rather remarkable. Not many people know about them. What they did was to take electrons of about 50,000 volts energy and they fired them to go through collodion, beryllium, aluminum and aluminum oxide films a few Angstroms thick, and then they bent them in a magnetic field and measured what energy they lost. What they found was that they got a sharp maximum. Not too sharp, 15 to 25 volts, but very little below this. It goes smoothly down and you are perfectly right. The experiments indicate that 5-volt velocities are relatively infrequent. So that it is actually apparently experimentally all right, and collodion is not too far from a biological kind of material.

BURTON: Of course, this comment applies to electrons of about 50,000 volts.

POLLARD: That is right.

BURTON: In radiation chemistry a large fraction of the total effect is produced not by electrons of 50,000 volts but by electrons of considerably lower voltage. So we must ask: what about electrons around 150 volts?

FANO: I would tend to be surprised on general grounds if it turned out that a mechanism such as was discussed before was quantitatively important in the action of ionizing radiation. Vice versa, it is perfectly obvious that such mechanisms are the most important things in normal biological events where high energies are simply not available and the processes of life depend on visible light. So for these things, it is obviously quite important.

BURTON: In what I propose to say I may be extremely naive. But since I admit it is naive, correct me. You know the Penning ionization gauge, in which a gas at about 10^{-3} to 10^{-5} mm is present. A glow discharge can be caused to pass through by the application of a crossed magnetic field. For such an ionization gauge comparison of the current and the number of molecules that go through indicates that all the molecules are ionized. I think that such a conclusion is certainly correct within a factor of 2. At the same time, there is a very bright glow. I have a feeling, derived from this calculation, that there is a very high probability of production of the excited states which give this glow.

Such a glow is seen with methane, benzene, and presumably with other gases.

FANO: It is probably due to transitions between highly excited states.

BURTON: In the hydrogen discharge tube?

FANO: Yes. I mean the transitions cannot be among the low lying levels. Even in benzene the resonance transition does not radiate in the visible.

BURTON: You mean the glow itself is an evidence of the fact that it is not the low excited states that are being excited but the high excited states?

FANO: Yes.

KASHA: There is one thing that I disagree with, though, and that is Dr.

Fano's argument regarding distribution of excitation energy. It is just the thing that I think does not apply to the kind of molecules which Dr. Linschitz discussed. I did a little rough calculation and it seems to me that there are levels which are more often from 6 to 20 volts. Those levels in a molecule like this are essentially mutually interacting and anything you do up at 20 volts is going eventually to come down to 5, 6 or 7 volts and cause the photochemical effects which Dr. Linschitz discussed.

POLLARD: How did you get up to 20 volts?

KASHA: Well, I think Dr. Fano was talking about something happening at 20 volts from some higher energy radiation.

FANO: This funneling of energy into particular kinds of excitation is something that happens in materials which really have special kinds of structures, so that they are fluorescent. Fluorescent materials are the object of much study just because it is convenient to use them. But there is not much evidence that most of the biological tissues are like that. Most of the organic materials do not have appreciable atomic groupings with such special structure.

MAZIA: Couldn't this problem be approached experimentally by comparing the effects of ultraviolet and ionizing radiations in cases where you have a qualitatively distinguishable effect? For instance, you spoke of absorption in the ultraviolet by nucleic acid. If you irradiate nucleic acid with ultraviolet, the effects on its structure are detectable by losses in ultraviolet absorption. How heavily would you have to irradiate nucleic acid with ionizing radiation to detect these same changes? Have you ever picked them up?

POLLARD: Pretty heavily, I would say, to pick up an effect that way. But to lose the biological function --

MAZIA: I was referring definitely to Dr. Fano's question. If the energy had to be funneled in through the mechanism he was discussing would you be able to detect the same kind of effect with ionizing radiation?

POLLARD: You certainly don't. The striking thing about irradiating stuff this way is that you don't see any change until you put it in solution. The only thing we have done on this for the two cases where we had bovine serum albumin and hemoglobin. We have put them on a quartz slide, and we have examined them in the Beckmann apparatus. It is really very surprising how small the change is in all the absorption bands and yet such material is totally insoluble. As soon as you do shake it up and look at it a little in solution all the absorbing bands have changed. Here I am talking in a certain sense against myself. You can have a process which is happening in the inert molecule. It is when the molecule is called on to function that you notice the difference, and the first function it has to survive is the ability of going into solution or at least standing contact with water. If you simply irradiated a nucleic acid molecule in the dry state you would have to put tremendous amounts of energy in to see these effects.

KAMEN: Perhaps the most spectacular demonstration of the difference between low energy ultraviolet radiation and ionizing radiation is that of the photoreactivation of phage. If you deactivate phage with ultraviolet you can reactivate it with visible light.

POLLARD: Well, that is in the bacterium, don't forget that.

KAMEN: Yes, that is a most important thing to remember. If you irradiate with X rays under the same conditions, deactivation is irreversible. I presume this will hold for betas and alphas.

POLLARD: Incidentally, only about 70 per cent is reactivated, so there is 30 per cent that holds out.

KAMEN: But there is a qualitative difference between ionizing radiation and ultraviolet.

BURTON: One of the things that one must never forget is that in absorption of ultraviolet radiation the absorption is very specific. On the other hand, for ionizing radiation the absorption is completely non-specific.

KASHA: May I make one comment appropos to the remarks on water and its triplet state? One would be interested in seeing whether any picture can be given for a stable (excited) triplet state of the water molecule. There are two sigma (axially symmetrical binding) orbitals in this molecule. Each such orbital contains two electrons, one of which could be excited. But a sigma electron could be excited only to a sigma anti-bonding orbital, which would result in bond-rupture, or to a Rydberg orbital, which might result in ionization. However, the water molecule contains in addition several essentially non-bonding electrons on the oxygen atom. One of these latter n-electrons could be excited to an anitbonding sigma orbital. The excited state could be either singlet or triplet in such a case, and would probably be stable, i.e., the molecule would not dissociate upon excitation. This is one interpretation of a possible stable excited triplet state of the water molecule. Such a triplet state might lie in the near ultraviolet, in contrast to the normal transitions of the water molecule which occur in the vacuum ultraviolet.

LINSCHITZ: The lifetime would be very long for such a molecule, that is clear.

KASHA: Yes.

PLATZMAN: I have a remark to make about the triplet states -- not about their chemical role, but about their mode of formation. We have mentioned three different ways in which they may be formed. First, indirectly by internal intercombination transition from higher excited states. I am not going to discuss this. Second, by recombination of positive ions and electrons. I am not going to discuss this either. Third, directly. This I shall discuss. What I am going to say is tentative and crude; it came as a surprise to me and perhaps will surprise some of you. It concerns the over-all number of triplet states produced by ionizing radiation, including primary, secondary, etc. processes. We have often said what Dr. Fano said a little while ago, that quite a few triplets are produced directly by the very slow secondary, tertiary, etc. electrons, because when these move slowly enough they can effect singlet-triplet transitions. This, I think, is the general belief, but I don't think that it is true. Mr. Miller and I at Purdue have started a rather formidable project of trying to understand the over-all effects of high-energy radiation in helium gas, by a complicated type of what Dr. Pollard calls "bookkeeping". This work is still in its preliminary stages. But when Jesse found that the metastables in helium could cause increased ionization, we at least had something to aim at besides the value of W, namely, the total number of metastables compared to the total number of ions. We tried to estimate this and it turned out not to be very hard to do, at least crudely. The surprising thing is that most of these metastables appear to be singlets, not triplets. There is, in the case of helium, the possibility of two different types of metastables, singlet metastables and triplet metastables, and

Jesse, of course, measures both of them if they are both there. Our rough calculation indicated that the total number of triplet metastables is of the order of magnitude of several per cent of the total number of metastables. Most of the metastables come from higher singlet excitations following radiation. Although it is quite true that very slow electrons can excite triplet states, there are so few of them with just the right energy and the excitation curve is so narrow that, so to speak, they just hop right through.

Of course, this is for the case of helium. I will not predict it to be a general result.

MAGEE: I think helium is a most unrepresentative case.

PLATZMAN: I would be the last person in the world to say that helium is typical, but with regard to the total number of triplets formed, relative to ions, I doubt whether it is greatly different from other substances. But even our crude calculation taught us that it is dangerous to guess about these matters.

MAGEE: I think the molecular case is much more favorable for the formation of triplet states. There are more triplet than singlet states and they lie lower, and so you will always have one triplet state or another you can excite. In fact, for several volts below the lowest singlet excitation you will be able to excite the lowest triplet state. I don't see how the helium calculation applies to molecules.

KASHA: I agree with what Dr. Magee said. All you have to do is get into any triplet state at all.

PLATZMAN: But the number of triplets formed directly will, I believe, be small, because the excitation curve is so narrow.

BURTON: However, if the exciting electrons have energy less than that required to excite the higher state, they then can excite only the low states. This fact is of major importance for secondary electrons.

KASHA: Can't they have 12 volts, 10 volts, 20 volts? Anywhere in that range will excite the lowest triplet state that Dr. Linschitz was talking about.

MAGEE: Even lower. Three, four or five volts.

PLATZMAN: They have to have just about the right energy. That is the trouble.

MAGEE: I think you are over-estimating the sharpness of the resonance.

PLATZMAN: I didn't estimate it. That is one thing that is known. I used the actual cross sections.

KASHA: I should like to spend a few minutes discussing a problem which is always pictured as an extremely difficult one to consider: that of the potential surfaces of a complex molecule in its various vibration and electronic states.

One rapidly gets into hyper-geometrical space in such a discussion. However, by limiting the number of space parameters to three, namely two interacting normal vibrations of the molecule, and third, the potential energy, a rather illuminating picture can be drawn. I shall limit my remarks here to a mere summary, for this discussion will be published shortly in full in another place.

The potential energy surface which one generates from the parameters given above is an elliptical paraboloid: on a horizontal cross section, ellipses are obtained which represent the Lissajou interaction of the two normal vibrations; in a vertical cross section, parabolas are obtained representing the potential energy of a harmonic oscillator (in this approximation, i.e., dissociation is ommitted).

A succession of electronic states requires a series of such parabaloids in three-dimensional space in the present case, the minimum of each parabaloid corresponding to the zero-point electronic energy (roughly) of each successively higher electronic state.

Only two points remain to complete the picture. One is, if the essential bonds in the molecule are not broken, so the geometrical structure remains similar in various excited states (so that the same set of normal vibrations can represent the molecular vibrations), then there is a mutual rotation of the elliptical parabaloids in space about the common energy axis.

The result of the above effect is the production of an extraordinary region of interaction of two successive potential surfaces, representing two adjacent electronic states. This, I should say, is the main reason for the extraordinary probability of internal conversion in complex molecules.

Let me re-emphasize this, because the physicist familiar only with nuclear, atomic, and diatomic phenomena would not realize the existence and efficiency of this process of internal conversion in molecules. No case is known in which a pentatomic or larger molecule can emit from any but its lowest allowed excited electronic state. The internal conversions are thus usually about 100% efficient as far as re-emission from higher levels is concerned.

Another point worth mentioning, and again one which would perhaps surprise the nuclear-atomic-diatomic physicist, is the limited number of low-lying electronic states in relatively complex molecules. For example, in benzene, there are only three excited singlet and three excited triplet states below the Rydberg states, which latter lie in the vacuum U. V. region.

Combined with what I have said previously in this conference about relative probability of normal internal conversions and intercombinational (e.g. singlet-triplet) internal conversions (it will be noted that both of these are radiationless, the electronic energy disappearing as heat), the conclusion one can draw is that frequently all of the electronic excitation energy can end up in the lowest metastable electronic (e.g. triplet) state.

Thus, most molecules are not fluorescent, but most organic molecules are phosphorescent (of course, when studied under appropriate conditions), with a quantum efficiency which is complementary to the fluorescence quantum efficiency (if both are observed).

LINSCHITZ: This would mean that all the estimates of the singlet lifetime must be off by a factor of ten.

KASHA: Yes, that is very possible. In fact, the lowest singlet and the lowest triplet, if they radiate at all, are the only radiation levels in the molecule, and if the triplet does radiate then the intrinsic (natural), singlet lifetime is longer by a factor which corresponds to the quantum efficiency.

BURTON: You say the singlet lifetime would be longer than we think?

KASHA: Yes, the observed lifetime will be shorter than that calculated from the integrated absorption, as a result of radiationless transition to the triplet state.

BURTON: With regard to the long lives of the singlet states, it is pertinent to mention the work of Duncan at Rochester. He worked on things like acetaldehyde, acetone, etc. and, as I recall, it turned out that the half-lives for these excited states before fluorescence are greater than 10^{-5} seconds.

KASHA: They are 10^{-3} but you correct them for a quantum efficiency of 10 per cent. But they have not been shown to be singlet-singlet, and vibrational analysis of the vapor absorption indicates that there are two electron transitions, remember. There is a school of thought, which includes me, which thinks that the lowest emitting level is actually a triplet and π antibonding.

BURTON: The point is, however, that the molecule must get into that state in some way or other.

KASHA: In fact, pyridine and acetone are rather analogous in their electronic systems.

BURTON: Is it the vapor state which you are talking about in the case of pyridine?

KASHA: The transition takes place in any state. The emission is observed only in rigid glasses or solid material.

BURTON: I was talking about gases here.

KASHA: There is a trivial detail. The intrinsic lifetime is 3.0 seconds. So you cannot observe this in the gas, but in the case of ketones you can. It happens to be 10^{-3} seconds and it can be 10^{-5}, but the quantum efficiency comes in.

BURTON: If you have such a long lifetime for your emitting state then, since the singlet state was presumably formed in the absorption act, the singlet emission must be a slow process compared to the other processes in which that state can be involved.

KASHA: The singlet-singlet emission would be about 10^{-5} or 10-6 seconds. The emission is not observed, but the decay constant is calculated from the observed singlet-singlet absorption curve.

LINSCHITZ: I didn't make myself clear a little while ago when I asked about the lifetime of the excited singlet. The point was not that the lifetime is shortened by the conversion to triplet but that in so many cases the maximum singlet lifetime is already so short that no appreciable conversion to the triplet can occur. If you calculate the singlet-singlet lifetime just from the absorption you get a radiative lifetime which would be an upper limit for the actual lifetime. Then you come out certainly with something much shorter than 10^{-7} sec., but you need this much time for the singlet-triplet conversion.

KASHA: In what case do you mean?

LINSCHITZ: Take a dye.

KASHA: Possibly I should mention an additional point. Many molecules in which the fluorescent lifetime is of the order of 10^{-8} or 10^{-9} seconds successfully emit with the smaller conversion to the triplet states. Most of the aromatic hydro-carbons fall into that category.

For example, in anthracene most of the emission is from the singlet, and it is extremely difficult to observe the triplet.

LINSCHITZ: How about Gilmore, McClure and Gibson?

KASHA: The cases where very high phosphorescence yields are obtained are those usually involving n ⟶ pi transitions.

KAMEN: What you said was that undoubtedly in a solid peptide where you have transition from the triplet to the ground state you might get a concentration of this extra energy in some sensitive spot. Would this happen with a peptide in solution?

KASHA: I would put it this way: Suppose we take something for which the lifetime is known. Let's say, pyridine -- with a lifetime of three seconds. Under what conditions can we observe the pyridine three second phosphorescence? I know of two. A crystal of pyridine or pyridine in a rigid glass.

There are two things which really complete the picture. In the fluid system or in an absorbed system, deactivation collision and reaction could very well have a higher yield or a greater probability, and so that could occur.

BURTON: Isn't there a possibility, for example, of a straight forward reaction of an excited polypeptide molecule with water?

KAMEN: Most proteins in the cellular systems are insoluble; that is, the active proteins. They are in the interfaces mostly, and water, which is supposed to be competing or giving reaction one way or another, may not be there at all in the case we are talking about. We keep harping about protein and water, but actually the cellular systems involved are insoluble systems. They are extracted as such. I doubt whether you should really worry about losing this mechanism because of the presence of water.

I think maybe you have something when you say that an inactivation could come about from migration of energy to this long-lived triplet state.

KASHA: There is one other point that I forgot to mention. It is perhaps the most interesting. What causes singlet-triplet transition? Well, there is a basic process, spin-orbital coupling, which is involved and by which such transitions occur. This can be enhanced by external electric or magnetic fields. One way in which this can be done is to replace the atoms in a molecule with heavier ones.

KAMEN: Can you give a specific example of this?

KASHA: Yes, for example if you take benzene, one way of increasing the atomic number of a critical part of the system is to put in a sulfur. There you have gone from an atomic number of -- well, that of oxygen to sulphur, from 8 to 16. The Z ratio increase of two causes an enormous increase in spin-orbit coupling.

In addition to that effect, which is internal, you can simply replace a hydrogen by some heavier atom and here you have a wide range of substitutions that are possible. You can go up to iodine, for example. This causes a tremendous effect. 10^{-5} is the order of magnitude of the enhancement of the probability for going from singlets to triplets, but the astonishing thing is you can remove the bond and it still happens. In other words, you merely have to lay benzene on a heavy atom surface or near a paramagnetic atom or molecule. The most common is the O_2 molecule. You can show enhancement of the singlet-triplet transition in many different ways and with catalytic effects that are remarkable. And it is possible that in some biological systems the presence of iodine or sulfur in the molecule or molecular oxygen near a molecule will cause a catalytic effect which will make the triplet state more effective, if there are any restrictions against producing it.

KAMEN: We have a good notion of some ways of explaining the effect of radiation as such. How would you explain the effect of radiomimetic substances? I am not asking for an explanation. I am just remarking that there are things you can do with agents like nitrogen mustard which simulate remarkably the effects of radiation, -- ionizing radiation in this case. What would be the mechanism using such radiomimetic molecule, if you assume that the radiation acts at an aromatic site like this? I must confess that I am stumped by it. You can show that some of the oxidizing enzymes which are affected by radiation are similarly affected by mustard.

BURTON: What happens in the cases you mention is that you are getting a nitrogen mustard effect similar to the effect produced by radiation, whereas Dr. Kasha has been talking about the removal of the effect which one might expect as a result of irradiation because of the presence of these heavy atoms.

KASHA: No, what I said is that this enhances the production of the triplet states.

MAGEE: This retains electronic energy in the system for long periods of time.

BURTON: What you are looking for is a connection with a theory for chemical action.

KAMEN: You have to get to where these two kinds of agents are about to converge. Now what does a nitrogen mustard do in making an effect like radiation? Any change in the cell enviroment very often can simulate a radiation effect. I don't understand it.

POLLARD: It is tough. I agree with you.

BURTON: Of course, one of the things Dr. Kasha was talking about all the time was going from the high singlet state to the lower triplet state, but it is also possible, if there is a reaction which is a producer of energy, to go from a high vibrational level of a low singlet state to a low vibrational level of the triplet state. This is particularly true if there is something present that favors or induces the transition. If there is some kind of exothermal chemical action so that the system can proceed from a low singlet state to a high triplet state, it is also required that there be something present which promotes transition from the singlet state to the triplet state. A mechanism must be provided for the transition from a high triplet to a low singlet state and from a low singlet level to a high triplet level.

Suppose we set up a situation (I am deliberately not specific) in which some kind of a chemical reaction occurs, so that in some way the molecule of interest proceeds to a high level of the ground singlet state.

KASHA: Oh, the ground singlet. Then you cannot get over to the triplet in general.

BURTON: You cannot get over unless there happens to be an interaction.

KASHA: That is right.

BURTON: Suppose there is an interaction. In these particular cases you happen to have atoms around which will promote the transition. That is all I was saying.

That is a mechanism for the radiomimetic effect mentioned by Dr. Kamen. What can be done with the idea I don't know.

KASHA: Incidentally, there is only one electronic system which I think the spectroscopists know in which most often the ground state does intersect with all of the excited states and that is the system which includes an ethylenic double bond. At least you can say that no one has ever observed any emission. No matter what electronic state is excited in ethylene you finally get hot ethylene in the ground state and the photo processes are almost identical with the thermal processes.

LINSCHITZ: There is a possibility that proteins may act to increase the lifetime of triplet states, by decreasing the chance of thermal quenching. In a highly organized protein there may be enough internal interaction and cross-linking to establish a rigid structure and impede vibrations. Triplet states excited in molecules within this framework, or closely associated with it, would be stabilized since internal conversion to the ground state would be impeded, as in the case of molecules which show fluorescence or phosphorescence only in rigid solvents or when they are absorbed on suitable materials. By this means the excitation energy may be preserved intact, as electronic energy, possibly even as long as the natural radiative lifetime of the triplet, and the chance of chemical reaction is thus enhanced.

KASHA: In that special case a pseudo potential is introduced into the molecule by the environment which prevents the normal crossing of the excited potential surfaces and the ground state.

PLATZMAN: If I understand the situation correctly, Dr. Kasha suggests that in certain kinds of molecules there occurs internal conversion of all types of excited states to long-lived states and, therefore, states in which the energy is chemically available. Just exactly what kinds of molecule? Dr. Kamen suggests all cellular proteins. This seems likely. On the other hand, we all agree that simple systems like pure H_2O do not qualify. Well, in general can we all agree upon the cases where this long-lived chemical availability will pertain because that, of course, as Dr. Kamen says, is extremely important.

KAMEN: Sterols and pigments should be added to the protein.

KASHA: I would say as a general rule any molecule which has a double bond in it and which does not contain an ethylenic link between that double bond and the rest of the molecule, will have stable triplet states. You see, there is the complication in the case of complete conjugation through an ethylenic bond which leads to total degradation of the electronic energy as heat.

BURTON: This is interesting. It ought to be possible to produce a mechanism of protection, shouldn't it? If one can provide for a resonance transition from a molecule that you want to protect to some other molecule containing an ethylenic linkage, then it should be possible to go down all the way to the lowest state without any decomposition. That would be a new case of sponge-type protection.

What you do is to introduce a molecule there in which there is a high probability of the type of resonance transition that Dr. Linschitz was discussing before, a high probability of such a resonance transition to a molecule in which there is an ethylenic linkage. Then the latter molecule, excited in this way, degrades very rapidly to the ground state without resultant chemical effect.

POLLARD: It does not work biologically.

BURTON: It has been tried?

POLLARD: Anything you do with a good biological protein stops its function.

KASHA: There is one place where Dr. Burton's suggestion has been exploited in a practical way. Plastics decompose with light. There is a photostabilizer -- this is just sort of backward -- in which the triplet state is produced with the probability of unity and what seems to happen is that the light is absorbed largely by the big chain molecule; that is, energy gets into this stabilizer which then goes to its triplets and just gives out its heat, and so it does remove the energy which normally cause the breakdown of the plastic.

KAMEN: What is the reference on that?

KASHA: Burgess (23).

PLATZMAN: Does the lowest excited state ever go to the ground state?

KASHA: I think it is very rare and, incidentally, internal conversion to the ground state I think is fairly rare in most molecules which are not ethylenic but occasionally it may happen. If it is a quantitative matter only, as I tried to indicate, then if the lowest singlet state is close to the ground state, it may actually degrade.

PLATZMAN: In my opinion, one must be more than a little wary about identifying chemical availability and chemical effectiveness of energy with the existence of a low triplet state.

KASHA: If the triplet state is an emitting state then that would be available energy, I would say. In other words, in this suggestion of Dr. Magee's about water, I think the most interesting thing to do is to see whether you can get luminescence of ice due to that triplet state.

IMPORTANCE OF RADIATION CHEMICAL EFFECTS IN RADIOBIOLOGY

Martin Kamen

I thought what I would do would be to go through my notes and attempt to recapitulate briefly what has happened at this Conference.

On the first day we were told about some recent findings concerning stopping power of various media for various radiations. Actually this is not a matter of primary interest to radiobiologists. The only immediate field in which this subject may be of interest relates to dosage and dosage units.

Among the topics discussed on the first day there was some mention of change in the value for the mean energy required to produce an ion pair in any given gas. As long as air is not mentioned nobody is perturbed. The whole system of dosage units depends on the measurement of the mean energy required to produce an ion pair in air. It does not have to, but it does. Because the clinical radiobiologists tenaciously cling to the roentgen as a unit for X ray measurement it is going to be necessary to pay some attention to what the ion-pair energy is in air. As noted here, it seems that the major differences have been found in the rare gases, and that these differences, which are quite large, arise from the presence of small amounts of impurities. By some strange chance, the standard medium chosen by the biologists for dosage happens to be one of the most impure things known -- air. So the probability that an impurity makes any difference in any further determination of the ion energy is quite nil. Maybe the extension of these same types of measurements to air may show differences, but it is doubtful. So I don't think we have to concern ourselves with any possible developments in this direction. This is my opinion and if anybody thinks differently he can certainly say so as we go along. I don't want to give the impression that this is going to be a steam-roller type of lecture.

ZIRKLE: I think you do us biologists a slight injustice in blaming us for the roentgen. We have accepted it as a necessary evil in estimating the energy transferred to tissue.

KAMEN: I think you are right. My choice of words was unfortunate. What I mean is that there is no way of getting around using the r at the present time.

There is a great paucity of data about what happens when electrons are slowed down to various low energies, and inasmuch as we do not know at the present time what fraction of the total track is effective in radiobiology it may be of some importance to determine just how much time an electron spends in lower energy states. Roughly, I think one would say that the chance of getting something to happen at a particular place depends upon how much time the electron is around there, and it is obvious that most of the time the electron spends is in the lower energy region. So since there is little known about the penetration of such electrons, there is an extremely deplorable gap in the data. It is a good thing that Dr. Pollard and others have begun to try to get data on the penetration of slow electrons. It is still very difficult but nevertheless it has to be done.

We need an answer to the question of the effect of chemical binding, either primary or secondary, on the career of slow electrons. That probably is another complication which may eventually be included in the treatments which have been given by Dr. Platzman and Dr. Magee. The work of Thompson (1) is extremely interesting in that you find small effects of chemical binding with such radiations as high-energy protons. However, I fail to see how these phenomena can be related at present to the questions raised concerning slow particles.

For the most part I think that we ought simply to review the situation as it stands now with regard to the essential mechanism of radiation interaction. It is agreed this involves mainly glancing collisions or gradual attrition. This results in dissipation of energy in small driblets corresponding very closely (within a factor of 2) to the average binding energy of the electrons in the atom. The end result is that in gases you get ion pairs corresponding to the dissipation of energy in very small amounts by comparison with the initial beam energy, and, in fact, the ion-pair event, except for the distribution, has no memory of what caused it. It is just the result of a glancing collision and it is a matter of chance where it occurs. The idea is that the only difference between various radiations is in the distribution of these events and the hope is you can explain differences in biological effects of various radiations by differences in distribution.

In the gas we usually talk about partition between ionization and excitation. This is certainly an erroneous assumption with regard to liquid, but it has been made in most radiobiologists' discussions. It is customary to say that water vapor will require approximately 30 ev per ion pair and if we go to a liquid a good enough assumption is that the situation is as though vapor were compressed a factor of 1,000. For most of us, that was a perfectly good assumption until yesterday. It came as a revelation to me that there is some other way of thinking about it and I suppose it did to most of the biologists here. And so I think it should be emphasized again in this conference that probably the most important thing that has happened is a clear presentation of considerations which mark a tentative beginning for a study of radiation effects in liquids.

There appear to be two alternative mechanisms at the moment.

One approach implies that the electron leaving its parent ion, eventually produces an H atom at a very great distance from the ionization site. Corollary to this is the assertion that there is very little initial recombination. The other approach, which appears diametrically opposed, pictures the electron as penetrating a very short distance, say 10 to 50 Å, and then coulomb fields take over and lead to a high probability of initial (or as Dr. Onsager called it yesterday, "preferential"). This recombination gives a radical pair with very little separation in space as contrasted with the result described above.

In pure water the production of a single ion pair by itself is not going to give hydrogen or hydrogen peroxide, and in order to get these you have to have three or four radical pairs in close enough proximity so there can be a reaction. However, if the radical pairs formed close to each other are most likely to be dissipated producing H_2 and H_2O_2, I would think they would be less available for radiobiologic effects. It would seem that radical pairs formed at some distance from each other would be most effective, on this basis. All biological systems would correspond not to the situation in which we have pure water but rather scavenger present (protein, fat, carbohydrate, salts, etc.).

BURTON: There is something we must be very careful about, and that is an exaggerated emphasis on ionization. In this case we say the ion lasts a short time. However, we must never forget that there is simultaneously produced, at similar concentration, some molecules in lower excited states. These lower excited states have not been ruled out as not making a contribution. We want to bear in mind that we may yet have to modify the theory of the radiation chemistry of water very drastically to include such lower excited states.

The question is whether these lower excited states may enter into something new and may give an entirely different type of reaction. My feeling is that it is better to think of the energy distributed among the free radicals as kinetic energy of the free radicals and to think separtely about the residual energy in the water molecule which does not happen to dissociate.

You remember we have mentioned here the possibility that at these high densities of excitation there may be interaction between excited molecules. Two excited molecules may come together. You see, Dr. Allen was very careful when he outlined his presentation of the radiation chemistry of water (2). He spoke of the forward reaction as opposed to the radical reaction. He did not say that the forward reaction was not a radical reaction. He said this is all we observe. We must remember that there may be something in addition to radical reaction.

KAMEN: In talking about ions and radical pairs we are speaking only about water, and I want to emphasize that the present discussions cover only the case of water.

ZIRKLE: While we are still on water, did I understand you to say that peroxide is not of great importance?

KAMEN: I was saying that the concentration in which the peroxide is produced would not be important as compared with the radicals. Peroxide should not initiate a chain reaction in the concentration we encounter in clusters. It is going to be the OH that does.

FANO: I should like to ask a question at this point. If you have an excited water molecule which dissociates, would anybody care to make a statement as to the likely method? How far are the two radicals projected before they start diffusing? Would they go less than the molecular diameter or much more? If two parts break off like this how far do they go before the momentum is dissipated?

KAMEN: How big a molecule do you want?

FANO: H_2O.

PLATZMAN: About two molecular diameters.

FANO: That is, more than 1 and less than 10.

MAGEE: It has been demonstrated by tracer experiments (3) that H atoms which have a kinetic energy of 1-2 ev can escape 100 per cent of the time from the point of formation.

BURTON: But the H atom is a special case.

PLATZMAN: Water has an especially open structure, so that H atoms can get out even easier.

KAMEN: There is the other alternative that the electron is not recaptured by the parent ion.

FANO: There is the formation of a radical at some distance which amounts to the same thing in the end.

BURTON: It does not amount to the same thing in the end; certainly not for the radiobiologists and I will mention that later. There is a distinct difference.

KAMEN: The interesting thing, at least to me, is the reaction which is always written for electron capture in water going to OH^- and H atoms. It appears this is incorrect, even though ΔH is in its favor, because of the necessity for the dipoles to orient first. This is something I never heard of before and I guess nobody else in my particular bailiwick has ever heard of it. I think it is important to keep in mind that as far as those of us who have to teach radiobiology are concerned, we have to try to teach the truth sometimes.

ONSAGER: A dielectric constant of 5 may be just enough to stabilize the hydroxide ion. The question appears to call for more experimental and theoretical work.

PLATZMAN: According to the model, a minimum of 2 electron volts is needed suddenly -- perhaps as much as 4. If my calculation is right, the atomic polarization won't help.

ONSAGER: Do you mean a dielectric constant of 5 isn't enough? That is 80 per cent of the self-energy.

PLATZMAN: This is a possibility, of course, but, thus far, the calculations indicate otherwise.

KAMEN: I would like to turn for a moment to consideration of protein in connection with these remarks on dielectric effects. Protein is actually quite a polar substance; it has a lot of free rotation and there is plenty of opportunity for all kinds of motion in a protein as a result of electrostatic forces. There is motion in the sense of continuous oscillation. Moreover, it is constantly being broken down, and reconstituted and this is one of the things about protein that is remarkable.

POLLARD: This is not true for the backbone. It is only true for the side chain amino acids. One must remember that. Schoenheimer's work is nice, but it concerns only the turnover of the amino acids (4).

KAMEN: This contention that the backbone is not involved in turnover is certainly debatable. However, I don't want to get into a discussion of the turnover in protein because it isn't understood by anybody. Obviously, many radiation situations have to wait for an explanation of non-radiation situations. Thus, it should be remembered that protein inactivation can be achieved by changing pH or ion environment, as well as by irradiation. To continue, one mechanism for the denaturation of protein has been proposed by Franck and Platzman (5) based on the splitting of hydrogen bonds, resulting from the electric field that is set up by ionization, which persists long enough and is of sufficient intensity to rupture something of the order of 30 hydrogen bonds for each ionization. This is an enormous dissipation of heat locally. Its origin is different from that of the electrostatic effects produced by thermal ions, which are slow and involve changes in which the static dielectric constant comes in and provides very efficient shielding. The electrostatic effect produced by ionizing radiation is very quick and in a certain period of time operates with practically no dielectric constant and is therefore much more effectual.

The major thing about present developments is that there is beginning to appear a framework on which one can assess the facts that are available, which is something that is urgently needed. In radiobiology we have an enormous wealth of facts. Some of them are dubious and all of them have to be graded according to the investigators. But they do exist. You have no way of picking between them except when they diametrically oppose each other. It is very important, really, that we have some feeling that there is a rationale in the background somewhere.

With regard to the reactions which occur in biological tissue, it is important to remember how complex biological tissue is. We have heard it ad nauseam but we might as well hear it again. I think that all of us who have come from physics and chemistry into biology have come very optimistically and very enthusiastically and have been caught up short.

POLLARD: It is a lot simpler than I had expected.

BURTON: It should be made a matter of record that Dr. Pollard shook his head in the negative.

KAMEN: A major difficulty with the biological system is that a given substance inside the cell behaves differently from the same substance outside the cell. Consider a piece of liver. It has lots of the enzyme catalase in it and it is important in liver function. Now, irradiate it. Then take the liver and extract the enzyme and you have a nice protein which you can get out crystalline. When you have done this and then measured its activity, nothing has happened to it. On the other hand, if you take the same enzyme, as Forssberg (6) has shown, and irradiate it in vitro, either in the dry state or in the wet state, with the same dosage it is completely inactivated.

Of course, there are explanations for this, but the trouble is that this kind of phenomenon makes it dubious as to how to interpret what is going to happen in a cell, because not only does it depend on whether the enzyme is adsorbed on something or is in solution, it depends very much on what other things are around to react with it, and this leaves a situation which is not one for optimism but certainly has to be kept in mind.

MAZIA: When you are working with the living cell, you have a situation in which your system can replace the inactivated units rapidly, and so you may have all kinds of radiation effects which are without any biological significance, and are not detectable unless you are able to set up special experimental situations to detect them. Radiation chemists sometimes study radiation effects on enzymes, but it is by no means certain that inactivation of enzymes is of any great inportance in over-all radiobiological effects.

KAMEN: Apparently the system has a certain capacity for repair which is in addition to the protective effect of the other protein which is around the enzyme. So the radiation effect depends on whether it is metabolizing or not. There are many things you can say about radiation, some of which are fairly general. Thus, there always seems to be considerable delay before the effect of radiation is noted. Bombard a system with an enormous dosage and you have to wait a while before the effect is apparent -- the biological effect, that is.

ZIRKLE: That is due to deficient observation, I am sure.

KAMEN: The difficulty is you cannot think how to find out what happens in the very first micro-seconds.

ZIRKLE: There are no suitable techniques.

POLLARD: The other thing is to say that biological observation is extremely sensitive and you have to wait for the biological amplifier to take effect before you can detect. The mere fact that the biological system reproduces something many times later gives a tremendous sensitivity.

KAMEN: This situation is no different from that encountered in many kinetic studies where the primary reactions are so fast there is no hope of freezing them. Nobody has ever particularly worried about this. What you look for, therefore, in biological systems is something which you can relate to a model outside. One of the most notable cases, of course, is the case of the cooperation between pigments in photosynthesis. In the case of photosynthesis, it is known that there is an association of pigments, including various chlorophylls. Usually chlorophyll A is predominant. There are also carotenoids and other pigments, perhaps some in trace concentrations we don't know the existence of. In any case, the one pigment in the green plant which has the lowest ground state, that is, the longest wavelength for fluorescence, is chlorophyll A. Everything else has a shorter wavelength fluorescence including chlorophyll B. It turns out, and this is what you would expect according to what Dr. Linschitz has told us, that all the energy funneled in anywhere along the line finishes up in chlorophyll A. It is a major triumph for the radiation theory in that it predicts this result with regard to the functioning of the biological system. A complete job has been done by Duysens (7) on this. Also it is true in the case of bacteria where you have bacteriochlorophyll, which is not very well characterized in the organism. If you extract it you can characterize it, but all you get is one substance. In the organism, the absorption spectrum associated with this dye is rather complex, showing many peaks in the infrared around 870 mμ, 910 mμ, and so on. The extracted pigment has only one big, broad absorption displaced from the infrared toward the blue. The point is that you can send in light at any of these frequencies and yet the only frequency that is usable in bacterial photosynthesis, is the one that corresponds to 910 mμ, the longest wavelength. In every case the energy degrades itself to the lowest lying stable state available.

All this is only to amplify Dr. Linschitz's talk.

FANO: Who has found out all these things?

KAMEN: These are experiments by Duysens (7).

KASHA: I should like to make a correction in your statement. What Duysens observed is not exactly what you said but very close to it. A slight correction, if I may. He did observe that the only emission in those systems with many dyes present was from the lowest fluorescent state of chlorophyll A. However, we don't know whether that emission corresponds to the energy available for the photosynthetic act or whether the complementary part of the quantum efficiency not observed is responsible for the photosynthesis act. In other words, the quantum yield of that fluorescence is not 1; it is lower than 1. We don't know whether the 0.4 of a quantum efficiency observed is responsible for the photosynthesis or whether it is the 0.6 not observed that is responsible.

KAMEN: The important point here is that there is an efficiency for energy transfer which corresponds with what you would expect in synthesized fluorescence. That is the important point.

KASHA: May I make one more remark. At a recent conference, another very important observation was made: That was that the reversible bleaching of chlorophyll A in the absence of air, or oxygen especially, persisted for 10^{-4} seconds roughly. This is what Livingston reported. The significance is that although no one has ever found a long-lived chlorophyll, he has indirect evidence for it for the first time.

TOBIAS: It seems to me that the system studied by Duysens might be a very good one to test these mechanisms proposed yesterday for X rays, gamma rays, etc. I think what you would find would be that the photochemical efficiency there would be very low.

BURTON: When you were talking about liver and enzymes you pointed out that very frequently our difficulty is that we observe not the immediate effect but the much later observable biological effect. As Dr. Pollard pointed out, this fact is itself evidence of the great sensitivity of the biological system. This is not an unusual thing in chemistry. After all, it is a very frequent thing. You know that in kinetics we frequently observe not the primary effect but a very much greater effect, for example, the result of a chain reaction. We all know this, and lately we have been able to make inroads on the immediate effect by tracer technics, for example, to discover the radical which started the affair. Williams et al (8) have been doing such work with radioiodine, thus detecting the first radical produced.

Dainton (9) did similar work, producing polymers and determining what radical added in. This is a very cute technique. It is the type of cute technique that chemists have been using very successfully to find out something about this first step. The only reason I mentioned this right now is because the biologists (I don't want to appear critical and this is not intended to be that way) perhaps have been lazy in the way that chemists have been lazy. It has been so easy to observe the big effect they have not given much thought to going back and seeing whether there is any chance of observing the primary event, whether there might not be techniques by which they may be examined.

POLLARD: Biologists have been seeking the primary effect for a long time. It is well known from the work of Beadle and Tatum (10) that enzymes are produced by genetic action of some kind. What the radiobiologist is seeking is the radiation mechanism involving the thing that forms the enzymes. What you have to look for is not the effect on the enzymes but on the thing that makes the enzyme.

BURTON: But in this particular instance, Dr. Kamen told us of a case where the isolated enzyme would have a tremendous effect. The point is, is the liver shielding the enzyme or reproducing it?

MAZIA: The experimental problem is to measure the actual turnover of enzymes. This is something that the biological chemists would very much like to do quite apart from the problems that we are discussing. It is still too difficult. The difficulty arises from the fact that we don't generally have methods for quantitative assay of enzymes in the analytical chemist's sense of the term. We have to use arbitrary measurements based on catalytic activity.

KAMEN: I think we should avoid getting into questions of biological mechanisms because little is known about them. I think I can say again that the whole business of radiation effect is entirely dependent first of all upon what happens in the non-radiation system; for instance, nobody can tell us how protein is synthesized and, therefore, how radiation would affect the synthesis of protein.

POLLARD: There is a very interesting speculation as to how protein is synthesized and it looks pretty good; namely, that the bigger helix of the nucleic acid just encloses the protein and specifically determines its structure.

KAMEN: Well, nobody has a function for nucleic acid in the biological system. It is there, but no one knows why. This speculation about the connection between nucleic acid and protein is an old one. In fact, I am among the many who at times have written papers about it. But I don't think we should deal at length here with anything about which we know so little.

Let's put it this way as far as biological substances are concerned. What distinguishes the biology from the chemistry is the cooperative action of cellular substances, and certainly there is where you have to look for part of the explanation of radiation effects. On the other hand, the isolated system has to be studied first before it is possible to imagine cooperative effects. What is known about the radiochemistry of surface films or interfaces? Dr. Mazia knows about this and I think probably he is the only one here or one of the very few in the country who has experience with this subject. Since practically all of the biological systems we deal with involve interfaces and most of the activity of enzymes takes place between the liquid and the solid state, it appears quite obvious that data are needed on this. I wonder whether Dr. Mazia can tell us about radiation effects on surface films.

MAZIA: What impressed me first in the studies of radiation effects on surface films containing enzymes was their enhanced sensitivity to inactivation by radiation. The systems we have studied most intensively is a pepsin-albumin complex spread over water. We can maintain it at a pH at which the enzyme is inactive, irradiate it, then measure the rate at which it digests itself when we shift to a pH at which pepsin is active. A few hundred roentgens suffice for large scale inactivation. The interpretation of such experiments raises some of the questions that Dr. Kamen must have in mind. The film is a two-dimensional continuum having the mechanical properties of a solid or gel of monomolecular thickness. All the molecules are interlocked, and you no longer know how to define an individual molecule. Therefore, you cannot really specify the unit that participates in a single event of inactivation. It might consist of what, in a solution, would be many molecules and this may account for the seemingly high efficiency of inactivation by X rays.

The other important question is the relation of the proteins to the water in the system. By spreading a protein over water, you partially unfold the molecules, increase the area of protein that is in contact with the water of the medium, and reduce the chances that part of the material will protect the rest against radicals. Such situations might exist in biological systems.

Recently, Miss Blumenthal and I have attempted to evaluate the role of spreading as such versus the role of water by studying the inactivation of dry catalase films deposited on solid surfaces. We compared the inactivation of films formed by first spreading the catalase on an air-water interface and then depositing on glass with the inactivation of films formed merely by drying down catalase solutions on glass. By "drying" we merely mean a condition achieved in a desiccator over "Drierite". While the data are limited, it looks to us as though the preliminary spreading at an air-water interface greatly increases radiation sensitivity even though the protein is irradiated dry. We observed about 70 percent inactivation of such films with doses of 3000 r, as measured by the Victoreen meter. The catalase that had not previously been spread was not inactivated by doses available to us with our prehistoric equipment. We are told by people who know more about these matters that the actual value of the dose is not very significant because of backscattering from glass. Nevertheless, the relative results remain and suggest that there is something that happens when you open up and cross-link protein molecules at an interface which does increase their susceptibility to inactivation by high energy radiation.

KAMEN: It increases the sensitivity?

MAZIA: Yes. There is a question that I should like to raise for my own information. On several occasions during this conference, the idea of local heat effects has come up. This is one of the oldest theories of radiation effects and one which many of us have thought was no longer taken seriously. What is its status?

FANO: I think it depends on what you mean by local.

MAZIA: I am just asking. This is the first time in years that I have heard anyone discuss the so-called "point heat" effects.

POLLARD: We have given this a lot of careful thought (11). You can measure very carefully the thermal constant for inactivation, let's say, with the wet or dry phase. Which one would not matter in this case, but let's take the dry phase. You can predict what temperature increase would be necessary to produce inactivation in a certain length of time. Then you can calculate the rise in temperature of a molecule due, say, to one primary ionization being put in there and it is plenty high. It goes up to 450^o or something like that. But in order to inactivate with the same inactivation constant (and this is the question which may be doubtful) the time that it would have to be kept there is something of the order of 10^{-2} or 10^{-3} seconds. There is no mechanism that I can think of by which in the solid state there would actually be temperatures kept up that long. If you put in an ordinary thermal conductivity figure and estimate that way, the temperature disappears in time of the order of 10^{-7} and 10^{-8} seconds which gives a discrepancy of 10,000.

We have looked into this carefully. Not only this work I have described here, but Appleyard (12) has done some on hemoglobin, Setlow (13) on catalase, and the conclusion is that the point heat theory applied literally as such cannot be entertained. However, it does seem to me that there is possibly what might be called "prepartition" heat. In the case of radiation the processes that occur before complete partition may well give you a reaction constant that is lots faster, and I am inclined to maintain that in that time between incomplete partition and full thermal action is a place where there is radiobiological action. I feel that some radiobiological action is concerned with that but not with heat.

MAZIA: Would the reaction system you are describing be dependent on the solid state?

POLLARD: That is right. You mentioned that there is a possibility that the interface holds up the heat and provides a mechanism by which you can have a little time. Then I think you do possibly bring in this process, as pre-equipartition or possibly as pure thermal.

LINSCHITZ: I should like to comment on this. The actual time required to bleed the energy away from a given site is clearly very sensitive to the degree of coupling of the original site with the rest of the system. Suppose that a given bond or group is initially excited electronically. This may occur, for example, in a single carbonyl group of a ketone, or the benzene ring in an aromatic compound, in which the electronic excitation is well localized. Upon internal conversion, this energy is changed to vibration which initially is also localized. Bonds immediately adjacent, and strongly coupled, to this site will be violently strained, and if such bonds, directly in the path of energy degradation, happen to be much weaker than those in which the vibrational energy is first released, the chance of rupture may be quite high. Bond breakage caused by such a specific process, in which the necessary energy is initially locally available, is hardly comparable to the corresponding thermal event. In this connection I would like to cite once again the early work on monolayers of stearic acid anilide, in which electronic excitation of the aromatic component of the molecule led to hydrolysis of the peptide link, with quantum yields of 0.2 or possibly even higher. Very little is known of the systematics of such energy migration and degradation, and more experiments on model compounds would be most useful.

FANO: Maybe it might be a good thing to avoid the confusion that is arising now by refraining from referring to vibrational energy as heat.

PLATZMAN: The difficulty is that, practically, there are no other words. I think that what Dr. Pollard said is very important and without question it is right; that is, you always do get some "heat", "prepartitioned", and, therefore, "local heating" undoubtedly modifies the action of everything we have been talking about the past two days. It isn't either/or. It is always both and you cannot have one without the other.

FANO: It is not heat.

PLATZMAN: I agree. But can you find another word to describe it?

FANO: Call it excitation of vibration.

PLATZMAN: This is a diffuse but highly non-equilibrium vibrational excitation of (part of) a large polyatomic system. I have a good deal of respect for the word "heat". But we don't have a word for the other, and "heat" is not a bad approximation until we do have, provided that it is properly understood as Dr. Pollard stated it.

POLLARD: I should like to state a little different point on the monolayers. Smith, in our group, has been doing some work on catalase. It is not yet complete and I do feel that in deference to him we should not say too much about it. But briefly it is this: He slipped lucite in and out of a trough that had a monolayer of catalase on it. This, of course, gave a monolayer on the lucite. Then he exposed it to the action of X rays and water as pure as he could get. To his surprise very high amounts of radiation were necessary before any inactivation could be observed. Perhaps 100,000 r produced no effect. He now has an effect. After something like 350,000 r the effect is of the order of 50 per cent.

If the experiment is right, the interest in it is that the lifetime of whatever is produced in the action turns out to be probably less than 10^{-4} seconds. By this means one can get some sort of estimate. This isn't the final word. It was not especially compressed film. No particular monolayer technique was used. It was just an ordinary film of catalase on a Langmuir trough and dipping was done twice, I believe.

BURTON: May I say a word about heat which is not entirely semantics. Consider a purely monolayer reaction. For occurrence of any reaction the activated complex has to exist; the activated complex is a special configuration with a special amount of energy located in certain degrees of freedom. Frequently there will be one vibrational degree of freedom which becomes very important. This molecule is not characteristic of the whole system. It is an exceptional molecule, which exists with low probability in an ordinary temperature situation. However, for a chemical reaction, it does not make any difference from the point of view of what happens to this molecule, whether it happens to obtain this energy by picking it up from the background (and then you look upon it as an effect of heat) or it happens to get this particular arrangement of energy as a result of coming down from a higher level. The energy that is in it and the distribution which is responsible for the chemical reaction is precisely the same in either case, but the chances of ending up in this configuration may be very much higher coming down from a higher excitation level than going up from the ordinary temperature distribution. I think this remark is pertinent to what Dr. Fano was saying.

POLLARD: This is very tricky because the actual result of such reaction depends not only on the energy of formation of the activated state but also the entropy.

BURTON: It is correct that the entropy of the final activated state is less than that of the state from which it derived (by a transition). However, so is its energy. The fact is that in the transition the free energy does actually decrease so that there is no occasion for disturbance about the decrease in entropy in the process.

POLLARD: What you are saying is you have a different reaction kinetics for higher excitation. That is what I feel may be true.

KAMEN: In connection with the remarks about studying not only isolated molecules but also intact systems, I should like to bring up two observations: one fairly recent and one very recent, because they are typical and one can probably find many instances of such observations. There is the well-known effect of radiation on desoxyribose nucleic acid activity. It is a fact that if one radiates any system, bacteria coli, say, or phage, the nucleic acid in the cytoplasm is usually not affected very much by the radiation as compared to the desoxyribose nucleic acid (DNA). There is no hard and fast rule for DNA distributions. It is thought to be in the nucleus, but it turns up often in the cytoplasm. However, in those cases where it is in the nucleus there is a profound effect on the turnover on the desoxyribose nucleic acid.

Recently Kellner (14) has done a rather interesting piece of work. What he did was to use the phenomenon involving the light reversal of ultraviolet inactivation. He wanted to know whether there was some process which is extremely sensitive as regards inactivation by radiation, which can be reactivated by light. His contention was that if you have an effect which is reactivated by light that is more of a bona fide radiation effect than some other effect which is perhaps secondary. What he did was to look first at the growth behavior of the cell. He found that the growth was not affected much and none of the oxidative enzymes were affected much. Little that you could easily test was affected. Nothing much happened, in other words, except to the division rate. What was observed was a continued growth of the cell. The radiation effect did not begin until the cell found itself in the position of having to divide. Then something happened. This delay, of course, was caused by the fact that the division mechanism had been tampered with. But since the cell did not need this mechanism until it was going to divide, no effect was seen until it began to do so. The fact is in these cells growth goes on unchanged, there is synthesis of the ribose nucleic acid and also when you reactivate with light the division rate is resumed.

CURTIS: Whose work is this?

KAMEN: Kellner (14).

PATT: Did he observe an early effect on DNA?

KAMEN: That is the point I am coming to. Immediately after the radiation, he found the DNA synthesis stopped. Upon reactivation, DNA synthesis was resumed. This is a very interesting piece of work because it appears to be the first time somebody has found a process which is interfered with almost immediately. That holds out some hope. It came about only because of the use of the reactivation approach.

This may be another example of what Dr. Burton means by a new approach. We have to wait for new techniques.

PATT: Was there any change in the absolute amount of DNA?

KAMEN: No. There is actually an increase in the amount of DNA in the cell. These are growing cells and there is synthesis.

MAZIA: It is a convenient system. Because the turnover is so low P^{32} incorporation gives a pretty reliable measure of synthesis.

PATT: Hevesy (15) has referred to this type of mechanism for some time.

KAMEN: But it is the first time that anybody has gone back to the event rather close to the cessation of radiation.

PATT: An interesting point in this regard is the fact that rather early effects on DNA turnover have been detected in sites distant from an irradiated area.

KAMEN: The trouble is, of course (and this is where Dr. Pollard's question comes up, which was what is the function of the nucleic acid in general) that we don't know what they are doing in synthesis. With regard to measurements of nucleic acids one would like to know if it is the nucleic acids that are affected or the protein that is affected, and when we know something about the structure of the nucleic acids and more about the protein structure, we should know a great deal more about those things. There is no objection to indulging in speculation about what happens to such structures when irradiated.

To continue with some other points. There are experiments on irradiating together and separately an enzyme plus its nucleotide prosthetic group (and most enzymes have prosthetic groups). Very often you can take them apart and put them together again.

You can take the prosthetic group and irradiate it separately -- likewise with the apoenzyme -- and then recombine them. The total radiation effect which is observed is additive, that is, the per cents of inactivation for each part add up to what is observed for the two irradiated units recombined.

This brings up the question of what kind of damage could you do to a thing like a nucleotide which would not affect the binding. This recalls Sinsheimer's (16) experiments on irradiation of purines and pyrimidines which we discussed at our meeting two years ago. Sinsheimer mentioned isomerization and reactions at double bonds all of which were away from the presumed bonding site between the purine and the protein. So you can see in this instance an actual demonstration of the specific effect of radiation; that is, of the localization of the damage which we heard about in model reactions all day yesterday. This again is an observation which bears directly on the model reactions considered and there are numerous others one can bring up.

It has been requested that we elaborate yesterday's discussion about the "triplet state". Well, to go ahead. In spectroscopy one characterizes energy states by quantum numbers and one of them is the so-called "spin" quantum number.

It was originally introduced in order to explain spectral-line splitting in externally applied magnetic fields, and it is usually thought of in terms of a mechanical spin of an electric charge. This makes it possible for an energy state to consist in fact of a number of states which are slightly different in energy because of the coupling of this spin with other electronic forces. The spin is quantized for each electron, and the magnetic moment associated with it, in units of the so-called Bohr magneton, has a value of $\frac{1}{2}$. The number of states that are possible depends on the total spin. If the total spin of the system is s, then the number of states, or "multiplicity" is $2s + 1$. If the spin is 1, then the multiplicity is 3 and the state a triplet state. Two unpaired electrons give a spin of 1.

Radiative transitions are most likely to occur between states of like multiplicity. To get into a triplet state from a singlet state, one usually has to have some collision process. Usually an excited singlet state can have associated with it a triplet state. The question is how often do we get molecules in this triplet state, and of what interest is this to radiobiology? According to the discussion which you heard yesterday the chances are that after all the energy is distributed and you degrade it all down thermally, there may be left some energy which will be effective for chemical reaction. The energy which is available for chemical reaction must be that which is still in the molecule. It is at this point you expect something like the triplet state to be important because that may be the only thing left which will hold the energy in the molecule for a long enough time so that there is reaction of some sort. The only questions are whether there are triplet states, how many of them there are, what is the population in the triplet state as a consequence of irradiation and what is the time they live?

KASHA: All the things you mention are measurable, and that is what people are trying to do today.

PLATZMAN: That is to say -- for any simple molecule, but not for example for an enzyme.

KAMEN: With the more complicated molecules the chances of long-lived states increase. The life of the metastable state can be really quite long.

KASHA: I think there is a limit on the order of seconds.

LINSCHITZ: I don't think that one can refer to the "triplet state of a protein". Rather if you have one amino acid, let us say, which is coupled to the protein chain only by peptide bonds, then you can with fairly good approximation talk about the excitation energy of just the aromatic part of that amino acid. So that what you would be doing would be holding the energy in one of the amino acids.

May I comment on the actual yield of the lowest triplet state? The claim has been made that the quantum yield might be as high as 100 per cent starting from any excited state and coming down. I wonder if that point could be discussed. The very fact that you increase the yield of phosphorescence as you enhance the spin-orbit coupling in the molecule by introducing heavy or paramagnetic groups indicated that in the unsubstituted molecule you cannot get yields of the lowest triplet states of 100 per cent.

KASHA: This is a matter of the different types of electron systems which can be studied. If you study aromatic hydro-carbons, i.e. π -electron systems, you may get relatively small yields of triplet excitation which, in fact, go from zero to some value like 0.6. Then if you make heavy atom substitutions in π -electron systems you can enhance the triplet state yield by how much is left. If there was 0.4 left you come up to 1.

LINSCHITZ: Take the type of structures that lie on the range from zero to 0.6. A molecule like tyrosine, of course, would give you a good yield of triplet state. But then take something like tryptophan or histidine. What kind of a yield could you expect there?

KASHA: No one has studied those. Somebody should study the amino acids in this respect. But I know that the people who have done the yield measurements (and this includes myself) have studied the aromatic hydrocarbons as the chief group of molecules which allows that yield enhancement to be studied, and in those cases they have found, for example, in the case of naphthalene the yield is 0.01, but in iodonaphthalene it is about 1.0, so that there is a tremendous enhancement in that case. However, there are other electron systems like the n-electron system which means chemically, e.g., those containing a carbonyl group, and in those cases yield of the triplet state is about unity and you can do nothing to enhance it because there is no other energy available. That is all there is to it, as far as I know.

KAMEN: There has been considerable discussion and I think it is about time to ask what suggestions for experiments arise from all this. In this connection, I think everybody is equally eligible for suggestions. I should like to start the discussion merely by pointing out some things which appear quite obvious.

First of all, we have already had four or five specific suggestions. But in addition, I think it is important that there be studies made on the effect of partial and total unfolding of protein on surfaces using various kinds of radiation. The effect of low energy electrons on such aggregates would be especially interesting. Not alpha particles so much as low energy electrons.

BURTON: By low energy what do you mean?

KAMEN: Between 1 and 10 electron volts.

MAZIA: We have made some studies of the relation between molecular "folding" in surface films of proteins and their sensitivity to X rays. The concept of "folding" of proteins is now so vague that I had better describe the actual case. If a pepsin-albumin film is formed under a certain minimum pressure, its activity as an enzyme-substrate complex is retained. If the film is permitted to expand so that the pressure falls below this minimum, it loses its activity irreversibly. We argue that the decompression has permitted the unfolding of the surface-spread proteins to the point where the specificity of configuration that is responsible for its biochemical activity is lost. We can inactivate pepsin-albumin films with relatively low doses of X rays, when the films are at the minimum pressure at which they are active. If now we compress the films and test their sensitivity to X ray inactivation, we find that the sensitivity decreases in a linear fashion as the pressure increases. Of course, we are decreasing the area as we compress the film. In a sense, then, the "unfolding" of the film results in an increase in radiation sensitivity.

KAMEN: There is a great deal of evidence which suggests that the enzyme is stablized by its prosthetic group and also by its substrates, so this is another line of experimentation which opens up as a result of previous biochemical studies.

Another thing that occurs to me is that the state of enzymatic adaptation as affected by radiation is still unexplored. Studies have been made, of course, which show grossly that adaptation ceases when the cell is irradiated along with other radiation sensitive processes. That is, if you knock out growth you also knock out adaptation, but this is a crude way of going about it. There are serological techniques available which make it possible in principle to study the protein composition of the cell during the adaptation process. If you want the details, it is the work of Melvin Cohn and others (17), and while this is still in the formative stage, it indicates that it is not going to be impossible to look for precursor protein in the adaptive process.

The question arises whether the adaptive enzyme is built entirely from scratch or comes from a slightly modified precursor. So far it appears that in the absence of external nitrogen sources the cell breaks down the other enzyme completely and then builds the new enzyme from small units. The question is at what stage of this process can one drag out the intermediates to see what they look like. This is something for a combination of immunologists, biochemists, and radiobiologists to look into. All I want to do is to bring to the attention of this group the fact that this approach is feasible.

We ought to have more specific information on just what molecules in the biological system are expected to be sites for metastable states and, therefore, for chemical action and what the chemical action is. It isn't just a matter of saying you have chemical action. You ought to be able to say with some definiteness just what happens.

I might just refer to experiments of Weiss and his group (18). They have studied the effect of radiation of ultraviolet or X rays on the breakdown of desoxyribose nucleic acid at various dose rates and total dosage with different radiations and also under different degrees of aeration.

What they found, for instance, was that in the amino acid there was depolymerization and there was a fission of glycosidic links, liberation of free base, deamination, breakage of ester rings, and splitting of the ribonucleotide link. Everything in the molecule can be broken down by irradiation. So there must be lost of sites for the localization of energy. Also, the reaction change involves the whole molecule. Moreover they can change the ratio of these products by irradiating either in hydrogen or oxygen. They find that the relative frequency with which the phosphate is liberated from the phosphate part of the ribonculeotide link increases as you increase the hydrogen concentration.

ALLEN: These were experiments in dilute solutions?

KAMEN: I have forgotten, but I think they were.

GARRISON: Yes.

KAMEN: The fact is that they were able to get a variation in the yield depending on which radical was dominant.

ALLEN: That is natural, since he had a different radical.

KAMEN: But the point is that also in the cell you might have a situation in which the radical population changes from one part of the cell to the next and you could not simply talk about the homogeneous system and use that to speculate about the fate of the ribonucleic molecule.

There is need for more such studies and they are probably not too difficult to do.

There is a great need for study of what happens when a simple amino acid is irradiated. What kind of radicals are formed, for instance, and how do they react with the other radicals?

I brought with me a report on the previous conference held here two years ago and I have looked at it to see what has happened since then with regard to the points that were covered two years ago. At that time there was considerable discussion of the work of Hart (19) on the radical recombination yield for tritium betas as compared with alpha rays, and so on . . . The data showed that there seemed to be a variation in total radical yield depending on the ionization density. I understand that has changed now, and the total radical yield does not depend on the ionization density.

MAZIA: Will you say what this is, Dr. Allen?

ALLEN: You have no way of telling how many radicals may form and then immediately recombine back to water. Now, the number of radicals that produce any net chemical reaction seems to be about the same for all radiations. However, one would expect that the radicals that go back to water are probably more numerous in the case of densely ionizing radiation than they are in the case of gamma rays. If this is so, you have to say that the total radical yield appears to be larger for the densely ionizing radiations.

ONSAGER: Could I have a few minutes for elaboration of some most interesting ideas about nucleic acid, which Pauling had picked up in England just before he visited us? Pauling told us that the X ray data are compatible with a sort of double coil (See Watson and Crick (20)). There is purine or pyrimidine attached to every sugar. As far as I could make out, Pauling had just two kinds of purines and two kinds of pyrimidines. In each layer you would have room for one purine and one matching pyrimidine. Some efforts have been made to check that by analysis and so far the verification is encouraging.

KAMEN: What nucleic acid is this?

ONSAGER: I am not quite sure.

POLLARD: I think this is a preparation of nucleic acid which has been examined by X ray for structure.

KAMEN: The ratio of purine to pyrimidine has never been 1, exactly.

MAZIA: Pauling's model deals with DNA. It is a fact that the ratio of total purines to total pyrimidines in DNA is unity. This has been shown for many kinds of DNA. What varies is the ratio of one purine to the other, with a corresponding variation of the ratios of the pyrimidines to each other.

ONSAGER: There also would be the question of whether there would be as much of one purine as there would be of its matching pyrimidine. They can fit themselves pretty well by sets of two hydrogen bonds.

FANO: Could you explain to which one is the purine and which one is the pyrimidine and which is the matching?

ONSAGER: I don't know exactly how they go. They are just drawn like this and there will be two places for the hydrogen bonds.

MAZIA: James and I have measured the thickness of monolayers of DNA. We consistently come out with a value of about 22 Å, which is just about 1.5 times the long dimension of a nucleotide. We could not explain our results in terms of a single nucleotide chain, but the newer concepts of helices composed of more than one chain fit the measurements very nicely. I have consulted with Pauling about these film measurements, and he feels that they are consistent with the idea, which Dr. Onsager has just described, that when we speak of a DNA molecule we refer to a unit consisting of more than one chain.

FANO: Can you explain which dimension you are talking about?

MAZIA: The "long dimension" I referred to is the distance from the "edge" of the base, through the sugar, to the "edge" of the phosphate. The space occupied by a nucleotide is often pictured as an elliptical disc. The long axis of the ellipse is about 13.5 Å. We were not able to determine, in our monolayer studies, whether there was any preferential orientation of the base end or the phosphate end toward the water.

The measured thickness of the DNA monolayer is one and one half times the maximum thickness predicted for a single nucleotide chain. Pauling calculates the cross section of his helix and it comes out to the same value as the thickness of the monolayer -- 22 Å.

KAMEN: What about the protein? Where does it go?

MAZIA: I don't see how Pauling's molecule can react with protein or anything else that combines with DNA through the phosphate residues. He places the phosphates on the outside of a tightly packed structure.

POLLARD: He thinks it can be opened enough to include the protein. He does not think with straight nucleic acid he can do it but he thinks with protein he might. At least he did two weeks ago.

ONSAGER: The model would seem to suggest that the blue print is just taken out of the safe when it is needed.

MAZIA: That can hardly be so. We know that the blueprint is in use all of the time, although at a slow pace. We know this from the results of simple experiments where we remove the nucleus from a mature, fully grown cell. This cell cannot live for very long without its nucleus, and, so far as we know, the action of the nucleus depends on its use of what you have aptly called the blueprint. We are pretty certain on this point because another kind of nucleus cannot be substituted; the right blueprint is required.

KAMEN: It should be pointed out that there are more than just the four pyrimidines. There are in addition a number of isomers. That is, there are about three or four extra bases which come in, in small amounts, which are, nevertheless, always associated with the very purest sample you can get of nucleic acid. There has been, therefore, some slight flaw somewhere in the structure. You cannot have a perfect setup.

MAZIA: But in spite of all this variation the point still remains that the total purine to the total pyrimidine is a ratio of 1. That has not weakened with all the variations and proportions that have been discovered.

KAMEN: This is simply a repeating structure, a very simple structure, isn't it?

MAZIA: Not necessarily. Dr. Onsager's point was that the particular sequence of bases along one chain implied a complementary sequence along the chain that is paired with it.

KAMEN: Was there a corresponding pyrimidine for the purine?

MAZIA: A large number of analyses by Chargaff and others (21) indicates that the ratio of the adenine (a purine) to thymine (a pyrimidine) in DNA is 1, and, correspondingly, the ratio of quanine to cytosine and its substituents is 1. Watson and Crick (20) have recently shown that in a two-helix model of DNA only thymine will fit in juxtaposition to adenine, and only cytosine will fit with quanine. Since the double-standard DNA would demand these uniformities in composition, they argue that the experimentally demonstrated existence of these regular nucleotide ratios in all kinds of DNA strongly supports their model. What varies from species to species of DNA is the ratio of adenine and thymine to guanine and cytosine.

FAILLA: I am wondering what bearing the discussion of the last two days might have on photo reactivation. Has anybody any ideas on it?

BURTON: If a hypothesis is wanted, it is always easy to speculate. Consider, as has been suggested, that a "semi-terminal" effect of high-energy is radiation is the production of a triplet state which is fairly stable or, in more general terms of a state which for one reason or another is not able to lose its energy by radiation. (Let us call this state A). On the other hand, this state A may absorb energy (for example, ultraviolet light) and be excited up to a state (Let us call it B) which intersects a high vibrational level of the lowest lying single state. (I). This system is shown schematically in Figure 4. The transition from state B to the low-lying singlet state I may be more or less rapid, depending on the governing selection rules and the variety of possibilities for internal conversion. The important point to note, however, is that by optical excitation a possible path is provided for transition from state A to state I. This is a stablilzing process. The alternative, if we wait long enough, may be that state A would disappear by chemical decomposition (for example, in a rearrangement process to give ultimate molecules in a single elementary process). Perhaps it will simplify matters if we look at figure 1 which corresponds to the suggested model. For simplicity, I omit the ground covered by Dr. Kasha and include only those states consideration of which is required in this model for photoreactivation. Incidentally, it is importation to this picture that the

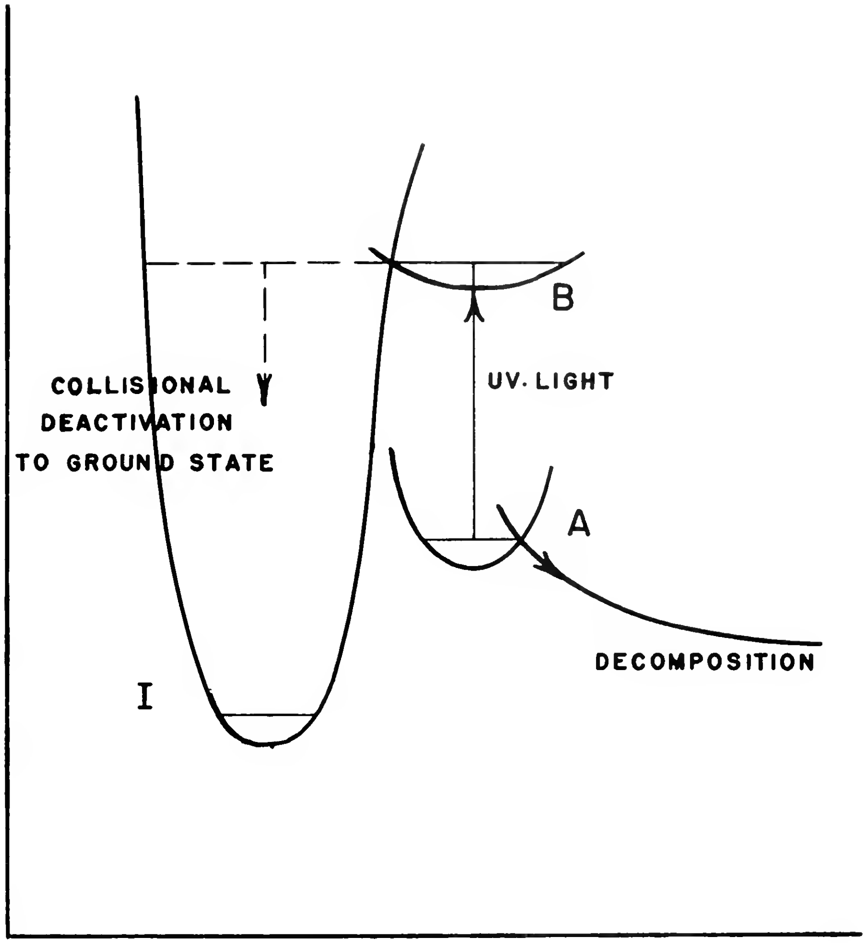


Fig. 4. Schematic Potential Curves for Photoreactivation Model.

"pallative" irradiation occur within the life of state A. How rapidly must the ultraviolet irradiation follow the irradiation by high-energy irradiation in order to have this protective effect?

MAZIA: As much as a day.

MAGEE: That is not impossibly long. You can have some odd configuration of a molecule. You remember I mentioned linear H_2O. You go to such a state and not the ground state of the molecule, and there can be a large barrier for going back.

KASHA: I think there are two things which tend to be confused here. I would say that there can be a geometrical isomer (which may or may not be a triplet) which radiates down in some instances, but if the geometry is extremely different it may not ever radiate down.

BURTON: Would those things last?

MAGEE: They might last a hundred years.

BURTON: Okay, there is your picture. The whole thing fits.

CURTIS: Is it really true that there is no situation in chemistry comparable to the phenomenon of photoreactivation?

PLATZMAN: No. There is, to cite one example, the bleaching of the photographic latent image. This has some features in common with bacteriophage photoreactivation, but the mechanisms may have nothing whatever in common.

CURTIS: I am afraid our time is up and we must adjourn. I certainly want to thank you all, on behalf of the National Research Council, for coming and participating in this discussion. I, for one, feel it has been a stimulating meeting and hope each of you has profited from it as much as I have.

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