NBS MONOGRAPH 12

Stabilization of Free Radicals at Low Temperatures

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

UNITED STATES DEPARTMENT OF COMMERCE • Frederick H. Mueller, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Stabilization of Free Radicals at Low Temperatures

Summary of the NBS Program

Edited by
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National Bureau of Standards Monograph 12

Issued August 1, 1960

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington 25, D.C. - Price $1.50

Foreword

The three-year Free Radicals Research Program, which was initiated at the National Bureau of Standards in September 1956 under Department of Defense sponsorship was terminated, as planned, on October 1, 1959. The status of the field of radical trapping and the accomplishments of the NBS-DOD program were reviewed and summarized in a group of seven papers presented at the Fourth International Symposium on Free Radical Stabilization in Washington, D.C., August 31 through September 2, 1959. These seven papers form the basis for this volume, which is the final report to the sponsors of the National Bureau of Standards Free Radicals Research Program. A cross-referenced bibliography of papers published as a result of the research completed during this three year period, and a summary account of the 1959 Symposium are also included in this report.

Although the first paper in this volume describes the general aspects of the technical management of the program, it is important to emphasize that much of the success and productivity of this program stemmed from the sympathetic understanding of its basic viewpoint by both the Department of Defense and the National Bureau of Standards. This basic tenet was that competent senior scientists provided with adequate research facilities, having freedom to choose their research activities, and relieved of administrative distractions, would achieve maximum productivity. Mr. Norman L. Klein of the Office of the Chief of Ordnance, Department of the Army, and Dr. R. D. Huntoon, Deputy Director, National Bureau of Standards, who had the ultimate responsibility for the program, were receptive to undertaking the research program in this way. It was only with their support, encouragement, and assistance that the research could be undertaken as it was, and the important roles that they played in the development and direction of this program are gratefully acknowledged. In addition, it is a pleasure to acknowledge the generous support of some twenty companies for their cooperation and participation in this collaborative enterprise.

There are many others who have contributed to the work of the last three years but the greatest credit for successful accomplishment must go to the research scientists. It has been their enthusiasm, their ideas, and their hard labor that has produced the results. However, without a smoothly running administrative services group and supporting staff, it would not have been possible for the scientific staff to have been so productive. Thus a special acknowledgement must be made for the competent and continuing assistance of Dr. Arnold M. Bass, under whose direction the administrative aspects were accomplished.

H. P. Broida
Technical Director
Free Radicals Research Program.

Contents

1. Organization and Rationale of the NBS Free Radicals Program

James W. Moyer[1]

In response to the advice of technical committees, the Department of Defense, in mid-1956, instituted a national program to accelerate the rate of learning on the formation and properties of free radicals. In addition to increasing the total contract effort in fields related to free radicals, it was decided to set up a central research effort for a 3-year period, for the purpose of pursuing new programs with maximum effectiveness and to disseminate widely the information and techniques. In particular, it was desired that there be as broad an industrial base as possible. By this means, if a striking advance should be made, the industrial laboratories would be in a "cocked" position, ready to shoot at development or semiproduction targets envisioned as possible followups.

The National Bureau of Standards was asked to carry out the "central laboratory" project theme by virtue of its research management capability, the interest shown there through some of the pioneer experiments, and the "neutral" atmosphere favorable to industrial participation. The program was launched in September 1956.

A program staffed by 30 to 35 senior scientists was conceived. In addition to the Bureau staff members and the enthusiastic associates from universities, about half the scientists were sent by industrial laboratories, their salary, travel and living expenses borne by their home offices. Thus, the project was actually supported by Defense and by Industry. Table 1 shows the companies participating during the 3-year period.

Each industrial participant signed an agreement to work on the Bureau Project as a "Free Radicals Research Guest" abiding by the Bureau's administrative procedures and agreeing to share information and research results conceived while at the Bureau. Ideas generated after leaving the Bureau were left for his company to capitalize on, thus providing additional incentive for prompt participation. This unique arrangement between Government and industry resulted in widespread interest not only in the technical area of the project but as a model for possible future cooperative research investigations of national importance as well.

The base of support for the project was, of course, spread more widely than U.S. Government and U.S. industry. In addition to scientists from three non-U.S. industries, much manpower came from universities and other establishments, here and abroad. These are shown in table 2. Table 3 is a detailed breakdown of manpower as the program developed showing NBS employees, industrial, university staff, and consultant affiliations.

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[1] Consultant from General Electric Company, Santa Barbara, California.

Table 1. *Industrial participation in the NBS free radicals research program*

Company	Scientist	Time at NBS
	Senior Research Staff	
British Oxygen Res. and Dev. Ltd	J. G. Waller	4/59– 9/59
California Research Corp	B. J. Fontana	1/57– 8/58
Callery Chemical Co	J. S. Hashman	1/57– 1/58
Columbia-Southern Chemical Corp	D. Kimpton	3/59– 5/59
Convair	T. D. Ling	9/57–12/57
Dow Chemical of Canada, Ltd	R. N. Barfield	1/57–11/58
Ethyl Corporation	J. T. Clarke	6/57– 8/58
General Electric Co	M. D. Scheer	5/57– 7/58
Grumman Aircraft Engineering Corp	T. Baurer	1/58– 6/59
Humble Oil and Refining Co	J. L. Franklin	4/57– 7/58
Koppers Co	E. L. Pascal	3/57– 6/58
Monsanto Chemical Co	R. A. Ruehrwein J. W. Edwards	11/56– 8/57 2/57– 2/58
Olin-Mathieson Chemical Corp	R. Klein	1/57–10/59
Shell Research Ltd	A. Thomas	1/59–10/59
Sinclair Research Laboratories	A. Chatenever	6/58–10/59
Space Technology Laboratories	M. W. Windsor	3/58– 9/59
Standard Oil, Indiana	A. Zletz	3/57– 3/58
Union Carbide Corp	F. I. Scherber	2/58– 5/59
U.S. Industrial Chemicals Co	A. Leifer I. Mador	9/57–10/59 5/57–10/59
Wyandotte Chemicals Corp	L. E. Kuentzel	12/56– 1/58
	Industrial Consultants	
Combustion and Explosives Research, Inc	B. Lewis G. von Elbe	5/58– 7/59 5/58– 7/59
General Electric Co	J. W. Moyer H. C. Mattraw	10/56–10/59 10/58–10/59
General Motors Corp	R. C. Herman	10/56– 7/59
Westinghouse Electric Corp	J. G. Castle	10/56– 7/59

Table 2. *Nonindustrial participation in the NBS free radicals research program*

Organization	Scientist	Time at NBS
	Senior Research Staff	
Catholic University of America	K. Dressler V. Griffing	11/57–10/59 2/57– 7/59
Centre National de la Recherche Scientifique	A. M. Pilon	10/56–12/56
Imperial College of Science and Technology	G. J. Minkoff	1/57– 2/58
Israel Institute of Technology	O. Schnepp	9/58–10/59
Université Laval	K. B. Harvey	10/56– 1/58
Université de Lyon	M. Peyron	3/57–10/58
Wayne University	B. Donn	12/56– 7/59
	University Consultants	
Brandeis University	S. Golden	12/56– 9/59
Catholic University of America	F. O. Rice	1/57– 7/59
University of Maryland	E. Montroll	4/57– 7/58

Table 3. *Personnel summary—NBS Free Radicals Research Program 10/56–10/59*

Date	NBS research staff		Non-NBS research staff		Supporting staff		Total
	Senior	Assistants	Industrial	University	Consultants	NBS	
10/1/56	[a]2 (½)	1 (1)	0	0	2	5 (4)	9 (5)
1/1/57	11 (9)	7 (7)	3 (2½)	4 (1½)	6	6 (5)	33 (25)
7/1/57	15 (11)	18 (16)	16 (13)	9 (5)	7	9 (7)	64 (54)
2/1/58	16 (12)	20 (16)	13 (12)	7 (5)	6	10 (8)	68 (52)
7/1/58	15 (11)	21 (13)	12 (10)	7 (3)	8	10 (7)	69 (50)
2/1/59	19 (15)	19 (15)	8 (7)	6 (3)	8 (8)	11 (8)	68 48)
7/1/59	12 (8¾)	12 (10¼)	7 (6)	3 (2¼)	3	10 (8)	44 (35)
Total number of people	25	37	23	10	8	13	

[a] Figures in parentheses indicate man-years.

To administer the NBS program, a special Free Radicals Section was set up in the Heat Division of the Bureau, with Dr. H. P. Broida as Chief of the Section, and Dr. A. M. Bass as Assistant Chief. Dr. Broida gave overall technical direction to the project, while Dr. Bass handled the administrative end. Bureau management cooperated to launch the program quickly by permitting speedups in normal procedures for the preparation of laboratory and office space, for the acquisition of material, and by creating niches in existing Bureau sections for many of the research guests. This was done with a minimum interference to other established research programs.

One important ingredient of the program rationale was the freedom of choice of research work on the part of each senior scientist. Participants were first chosen for their interest in the broad field and their established research competence, after which they were essentially unrestricted as to their experimental or theoretical approach. This procedure has become so rare generally that it seems worthwhile to examine how it worked.

The freedom given researchers contributed, of course, to a very high morale in the project. This was further bolstered by laboratory arrangements for working odd hours, nights, and Sundays. With such freedom, however, goes responsibility both on the part of the scientist and the management, to alter courses of action which, after a suitable period, appear to be nonproductive. Since all initial approaches were not equally effective (hidden difficulties soon came to light!) it was inevitable that some regrouping should occur. Such adjustments continued from the first 6 months almost to the program's termination.

In a research atmosphere devoted to freedom of choice, it is also the responsibility of the management to provide as many factors as possible in the environment to capitalize on the larger number of fresh ideas which accrue. To this end "cross-fertilization" techniques were instituted. Weekly seminars, partly with Bureau researchers, partly with outside guests, were instituted. A bimonthly Newsletter was edited and distributed by Mrs. Floyd Mauer. This Newsletter contained preliminary knowledge of research progress at the Bureau as well as heartening and informative items from many of the other laboratories throughout the world, contributed on a voluntary basis. The Newsletter circulation rose from 90 to 550, and its success was due to able and prompt editing as well as adherence to the printed policy of not permitting quoting or copying of such preliminary informal material.

Travel to attend meetings and to other laboratories was greatly encouraged and found to be especially stimulating. The Defense Department greatly assisted in much of this travel, especially for several of the project personnel to attend the 1958 Free Radicals Symposium in Sheffield, England. The Defense Department also gave special assistance to the travel requirements for many scientists from abroad to work or attend meetings at the Bureau, thus providing further stimulus.

Several of the industrial scientists carried their interests and new techniques home with them, starting up or enriching their firm's free radicals research. Out of the one hundred or more research papers to evolve, many are authored jointly by Government-industry teams.

The scientific content of the program is reported below. But it may be said here that a greatly increased understanding of low-temperature phenomena and techniques was one of the byproducts of the project. Liquid helium handling has now become routine, and because of the project, commercial Dewars of many special designs are now available at reasonable cost. Advances in the spectroscopic instrumentation art have been made, and X-ray and electron diffraction have been carried out on low temperature specimens. Liquid hydrogen handling techniques have also been improved, as well as means for production of intermediate low temperatures. As the program progressed, more extensive use was made of the powerful new electron-spin-resonance techniques, although there is much more to be gained in this application than the project time permitted.

That the program did not result in a so-called "breakthrough" for new rocket propellants should disappoint only the space merchants. The remainder of the scientific fraternity is grateful for a vigorous novel approach to team research which resulted in a flowering of the state of the art in a field of universal interest and importance.

WASHINGTON 25, D.C., November 16, 1959.

2. Qualitative Comments on the Physical and Chemical Processes in Trapped Radical Systems

C. M. Herzfeld and M. D. Scheer

It is clear from a qualitative consideration of the phenomena involved in trapped radical research that several general types of processes occur, either in a sequence or concurrently. One may list these types of processes in the order in which they occur, and so obtain a fairly clear qualitative picture of the events which take place.

First of all, free radicals must be formed. In the gas phase this may be done by electron impact in an electric discharge, or by heating the gas to high enough temperature to dissociate the molecules, or by optical methods such as photolysis. In the solid, free radicals may be produced by electric discharges, by photolysis, or by bombardment with nuclear particles or electrons. In many of these processes ions are formed as well as radicals (which are, by definition, electrically neutral). Not much is known about the importance of these ions in the processes we discuss, and our attention will be focussed primarily on the molecules and on the radicals produced in the ways which have been mentioned.

When the gas containing molecules and radicals (and perhaps inert diluent gases) hits a cold surface (in this work usually below 20° K), the gas condenses. Molecules, radicals, and inerts are all set down in a complex mixture. Many processes contribute to this result. The individual species hit the surface, some stick, others are reflected, some radicals react on the surface, some species wander over the surface and some diffuse through the solid. There may be gradients of concentration, temperature, mean energy, etc., within the gas and within the solid. The whole phenomenon and the structure of the resulting solid are certainly very complicated.

Radicals which are in excited states when they hit the solid, either radiate, or transmit their energy to the lattice. They may radiate from the surface or from the interior of the solid. The energy levels and transition probabilities of species in the solid are perturbed by their neighbors in the solid in ways which may be characteristic of the neighbors. Radicals (and molecules and inerts) will absorb radiation incident upon the solid, and the former will also often exhibit paramagnetic resonance absorption.

The manner in which radicals are trapped plays a considerable role in some processes. The trapping may involve just a "freezing in" at some position in the lattices (either in a substitutional or in an interstitial site), where the radicals are prevented from recombining simply by isolation from each other. Trapping may also be accomplished by formation of loosely bound molecules (not ordinarily stable) between radicals and molecules or radicals and diluents. The short range forces between all species will have important effects on these trapping mechanisms.

Whenever one has a system with more than one component, the question arises whether this system has stable thermodynamic phases. Also the equations of state of free radical systems may be significant in some cases.

Free radicals in solids may recombine and liberate energy. An increase in local temperature and in radical diffusion rates occurs, so that other radicals are liberated which in turn may react, and so on. Such radical chains may or may not branch. It is clear that branching processes lead to an instability in the system (explosions) because the number of radicals produced is greater than the number destroyed. Diffusion controlled flames may also occur in such systems. In addition, free radicals may react with the solid to produce radicals not originally present. These may either be stabilized or react further to produce other radicals without branching in the radical chains. If a continuous production of radicals is maintained, profound changes in the chemical nature of the original solid result. It is evident that the kinetics of this latter type of process depends strongly on rates of radical diffusion and the activation energies of the radical-molecule reactions involved.

Finally, after some time, the system returns to its equilibrium state.

The presentation of the results of the program at the National Bureau of Standards will follow this sequence of events approximately. In this way a rather detailed picture of the processes which occur can be built up, and one can then judge readily what parts of the whole problem are reasonably well understood, and where the largest gaps in our knowledge are.

WASHINGTON 25, D.C., December 18, 1959.

3. Experimental Aspects of the National Bureau of Standards Free Radicals Program

Milton D. Scheer

1. Radical Production Techniques

1.1. Production in the Gas Phase and Depositon on a Cold Surface

a. Electric Discharge

The most widely used method of generating gaseous free radicals at NBS has been the coupling of microwave power at 2,450 Mc to a quartz tube through which the gas under investigation is flowing at pressures in the region of 0.1 to 10 mm Hg [1] [1] (fig. 1). No significant effect of microwave frequency on the production of radicals has been found [2]. Usually about 10 to 100 w of microwave power is applied to the coupling resonator. The concentration of atoms and radicals in the gas stream flowing out of the discharge plasma is relatively independent of the power applied to the resonator. A careful study by T. Shaw [2] has shown that the fraction of H_2 dissociated to hydrogen atoms in a 3,000 Mc discharge increases somewhat with

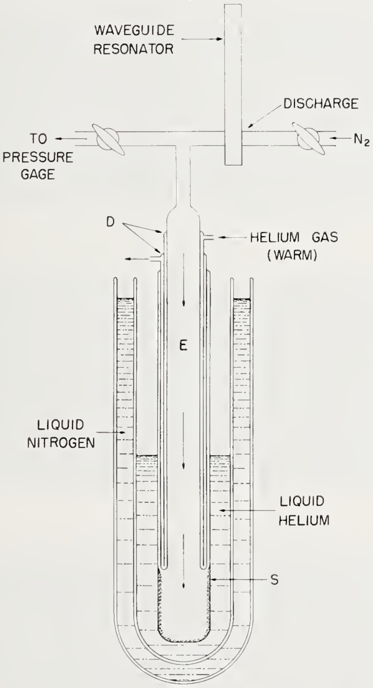

Figure 1. *A typical liquid helium Dewar used for the study of the condensed products of a microwave discharge through* N_2.

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[1] Figures in brackets indicate the literature references at the end of this paper.

increasing power and decreasing flow rate. The main advantage of using microwave power larger than 100 w is that a stable discharge can be maintained at higher pressures and larger flow rates.

The dissociation of polyatomic gases into radicals in an electric discharge is largely caused by energetic electron-molecule and ion-molecule collisions. Most of the electrons are formed as a result of the ionizing collisions which occur in the discharge plasma. In order to maintain the discharge, the rate of electron production must balance the rate of electron loss occurring at the walls of the discharge tube [3]. The question whether ions and electrons are important species at appreciable distances outside of the discharge zone is largely unanswered even though for simple gases like N_2 and O_2 the radiating species on the downstream side of the discharge zone are unaffected by large external electric or magnetic fields [4]. Microwave measurements of the free electron density in the afterglow region of discharged nitrogen have shown the presence of about 10^9 electrons/cm^3 which corresponds to about one electron for every 10^6 nitrogen atoms present [5]. The influence of these charged particles on the process of radical collection on a cold surface is unknown at present. Further, electronically and vibrationally excited species [18] are also present in the downstream side of the discharge, thereby complicating even further the process of radical stabilization on a cold surface. Thus, while this method of generating gaseous radicals can in some instances be made quite efficient (up to 90% for the dissociation of H_2), there is considerable uncertainty in regard to the exact nature of the gas which is finally deposited upon the cold surface.

The condensed products of discharged nitrogen have been extensively investigated at NBS in the 1° to 35° K region. The demonstration that ground state ^4S nitrogen atoms can be stabilized in such a solid is made quite conclusive in view of the spin resonance spectra obtained by many investigators. [8, 15, 17] (fig. 2). Interpretation

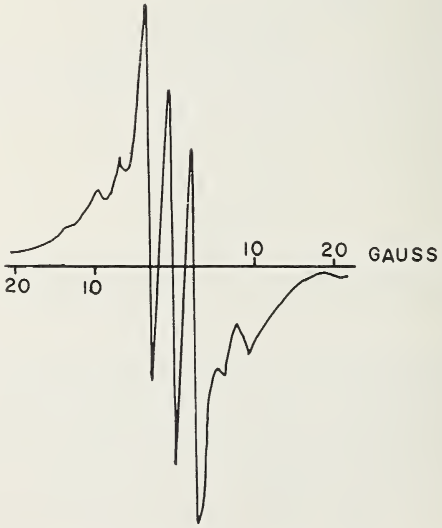

FIGURE 2. *ESR spectrum of ^4S N atoms in an N_2 matrix at 4° K.*

of the cold solid emission spectra has indicated that stabilized, excited N atoms interact with at least one neighboring N_2 molecule [6, 7, 9, 10, 11, 12] (fig. 3). Estimates obtained from magnetic susceptibility and electron spin resonance measurements have shown that the N atom concentration in the 4° K solid is of the order of 0.1 percent. When the concentration of atoms exceeds this value of about 1 part per 1,000, the solid becomes unstable, and phenomena closely akin to explosions can take place in this low-temperature environment [13, 14]. The radiation emitted during these "explosions" and during warm up of the solid is undoubtedly due largely to the recombination of the ${}^4S$ nitrogen atoms. However, the details of the kinetics of this process are far from clear at the present time. The appearance of intense Vegard-Kaplan bands $({}^3\Sigma_u \rightarrow 1\Sigma_g^+)$ has been tentatively attributed to N atom recombination in the solid. It is interesting to note however, that the first positive system of nitrogen $({}^3\Pi_g \rightarrow {}^3\Sigma_u^+)$ is

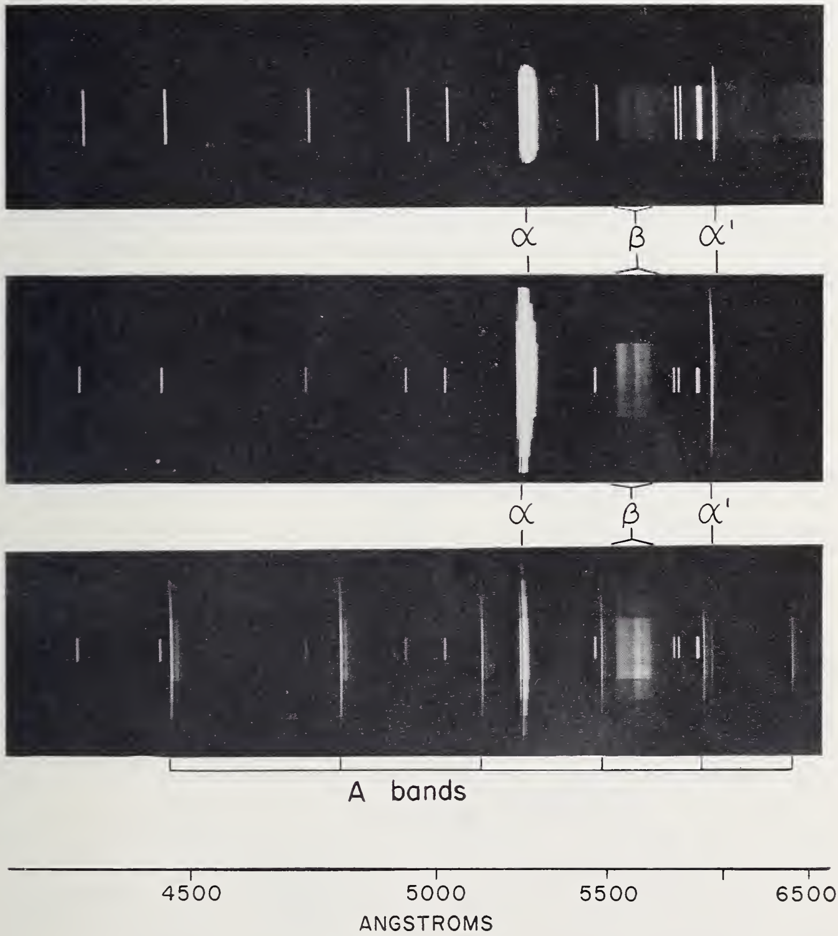

FIGURE 3. *Emission spectrum in visible region of nitrogen irradiated by 10 kv electrons at 4.2° K.*

not present to any appreciable extent in these flashes while it is one of the principal spectral features of the gaseous afterglow where N atom recombination occurs with a rate constant of 5×10^{15} cm^6 $mole^{-2}$ sec^{-1} [48].

b. Thermal Dissociation

The method of thermal dissociation is capable of yielding a well defined stream of molecular fragments provided that thermodynamic equilibration is achieved in the furnace source and recombination processes are minimized in the effluent gas. Complete knowledge of the identity and concentration of the species in the heated source is only possible if the complete set of thermodynamic properties is known for the system being investigated. The requirement is readily met for some of the simple diatomic molecules such as H_2, O_2, N_2, and the halogens, but for more complex systems complete thermodynamic information is generally lacking. In order to maintain the well-defined gas composition downstream of the furnace source, recombination processes must be avoided. This can be done in either one of two ways. Either molecular collisions are eliminated by collimating the effluent stream into a molecular beam, or by high dilution with some inert gas. The former is easily the most certain of achieving this objective, but it suffers the disadvantage that obtainable beam intensities are small ($\sim 10^{15}$ particles/cm^2/sec) so that only very small quantities can be deposited on a cold surface per unit time.

There have been several systems constructed at NBS in which thermal dissociation has been used to obtain molecular fragments in the gas. Two such pieces of apparatus using the molecular beam technique were designed, one for examining the deposition of I atoms on a cold glass surface, (fig. 4), the other for investigating the surface

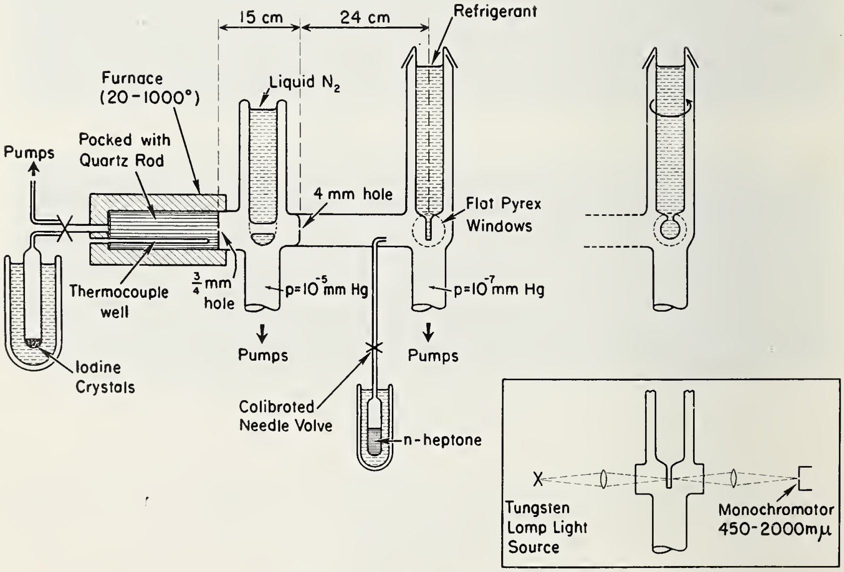

FIGURE 4. *Schematic diagram of molecular beam apparatus.*

migration of H atoms on a tungsten surface by means of the field emission microscope. The dissociation of hydrogen on an incandescent tungston ribbon has been used to explore radical producing reactions in cold solids [19, 20]. In attempts to produce a solid containing unstable molecular fragments, organic compounds have been pyrolyzed in a furnace mounted near a 4° K surface [21].

Evidence for the stabilization of solid free radicals produced in this fashion is rather meager. When a beam of thermally dissociated iodine impinges upon a 77° or 20° K glass surface, the predominant process is atom recombination on the surface. The pyrolysis of azoethane (highly diluted with argon) near a 4°K surface has resulted in the formation of *N*-butane after warm up of the cold solid. Infrared spectra taken of the 4° K solid, however, did not show the presence of *N*-butane or the ethyl radical for that matter. The irradiation of solid olefins at 77° K with hydrogen atoms has yielded large conversions to the alkane ($\sim$90 %), and the radical dimer ($\sim$10 %) However, an extensive search for stabilized alkyl radicals with an electron spin resonance spectrometer failed to yield positive results. It appears therefore, that efficient radical-radical recombination occurs in the cold solid under these conditions. The absence of a spin resonance signal indicates that less than 1 out of every 10^6 to 10^7 H atoms which react yields a stabilized free alkyl radical.

c. Gaseous Photolysis and Radiolysis

Of the possible techniques for generating radicals in the gas, the least promising and hence the least explored is gaseous photolysis (ultraviolet irradiation) or radiolysis (X- or γ- irradiation) prior to desposition. Since low-pressure gases in general are rather transparent either to ultraviolet or ionizing radiation, the generation of detectable radical concentrations is not possible unless very intense radiation sources are used. The possibility of rapidly pulsing a high-intensity flash lamp and depositing a molecular beam of the photolytic fragments has suggested itself to one of the NBS investigators [22], but shielding the cold deposit from the intense radiation source (in order to avoid ambiguities in interpretation) is a formidable experimental problem. In any case no serious attempts have been made at NBS to collect radicals generated in this fashion.

d. Deposition Process

The condensation of a gas upon a cold surface is one of the least understood of the processes which occur during stabilization of radicals initially produced in the gas phase. When a molecule strikes a surface it may rebound back into the gas after a single collision with the surface, it may become bound to a surface molecule for a time which is large compared to a single oscillation about the bond made before it escapes back into the gas, or it may migrate at random over the surface and coalesce in a process of nucleation with other such particles and become a permanent part of the deposit. The extent to which each of these occurs is not known for any particular system. A review paper [23] by S. Wexler on the deposition of atomic beams shows what measurements have been made of overall condensation coefficients defined as the fraction of the total number of particles striking a surface which remain deposited. In general, the lower the surface temperature the more efficient is the deposition process for a given species.

Measurements made at NBS of the condensation coefficient of argon on a 4° K argon surface yielded a value of 0.6 [24] while the condensation of iodine on a 77° K glass surface occurred with nearly prefect efficiency [25]. It is seen, therefore, that not only the surface temperature but the material being deposited and the nature of the substrate surface are of significance. In any case, a complete understanding of the stabilization of gaseous radicals in the solid state must be preceded by a more detailed insight into the deposition process. As an example of the complex phenomena occurring during deposition, M. Windsor at NBS has observed large temperature fluctuations in solid hydrogen and deuterium during deposition on a liquid helium cooled surface. Similar observations have been reported by B. Fontana [13] for the deposition of discharged nitrogen. Such observations strongly suggest the existence of large temperature gradients in such solids as they are formed by condensation from the gas. The effect of these gradients on the rate of radical recombination and the production of radical trapping sites is little understood at the present time.

1.2. Production of Radicals Directly in the Solid

a. Electron Bombardment and γ-ray Irradiation

Electron bombardment and γ-irradiation are probably the most widely used techniques for generating radicals in a cold solid. Irradiation of nitrogen deposited on a 4° K surface by 10 to 50 kev electrons has produced essentially the same emission spectra as that shown by the condensed products of an electric discharge through nitrogen [26, 27] (fig. 5). Bombardment by Co^{60} γ-rays of nitrogen, hydrogen, and methane condensed at 4° K has yielded solids which exhibit spin

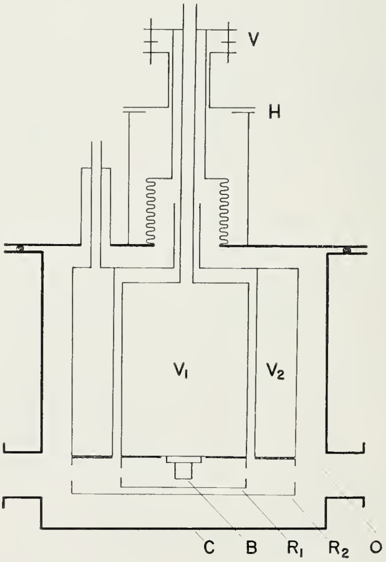

Figure 5. *Simplified vertical cross section of cryostat for electron diffraction experiments.*

C—chamber; B—copper block; R_1 and R_2—radiation shields; O—openings; V_1—liquid He vessel; V_2—liquid N_2 vessel; H—horizontal sliding mechanism; V—vertical adjustment screws.

resonance spectra of the N, H, and CH_3 radicals [17, 28] (fig. 6). Qualitative examination of the warmup glows from γ-irradiated nitrogen has shown the same spectral features observed in the other methods of generating N atoms in a solid nitrogen matrix [29]. In general it has been found that the irradiation of cold solids with ionizing radiation has been one of the more successful methods of producing stabilized molecular fragments, although the concentrations obtained rarely exceed 1 part per 1,000.

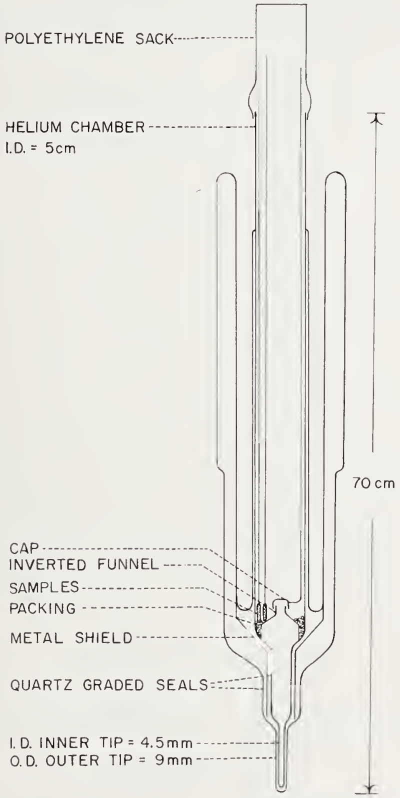

Figure 6. *Helium Dewar used in electron spin resonance experiments.*

b. Ultraviolet Irradiation

Ingram et al. [30, 31] have produced organic radicals in solids at 77°–110° K by photolyzing solid mixtures of H_2O_2 and various alcohols and hydrocarbons. These radicals have been tentatively identified by means of the hyperfine structure shown by the ESR spectra but no positive identification has been made.

Attempts to produce radicals by this method have been made at NBS. Conventional absorption spectroscopy was used for radical detection instead of the more sensitive ESR technique. Were these attempts successful (i. e., if the number produced were large enough to be detected), they would have provided independent evidence for specific radical identification. A typical case is the one reported by

H. Brown at the Sheffield meeting in September 1958, in which CH_3I was photolyzed at high dilution in an argon matrix at 20° and 4° K. Infrared absorption of the solid indicated that considerable reaction occurred, but the CH_3 radical was not detected. Jen et al. [32] performed an almost identical experiment but used ESR for detection. These investigators found the quartet spectrum at $g=2$ which has been attributed to the hyperfine interaction of the unpaired electron with the three protons in methyl. In essence, then, this method of generating radicals suffers from the same difficulty which appears as a recurrent theme throughout these investigations, namely that the concentrations produced are too low to be detected by any method except the most sensitive.

c. H-atom Irradiation and Subsequent Reaction in the Cold Solid

The possibility of providing two independent methods of radical identification for the same system presented itself when it was discovered that H atoms can react extensively with cold solids [19, 20, 33]. The addition of H atoms to solid olefins undoubtedly involves the primary formation of an alkyl radical [19, 20]. The presence of di-isopropyl and 3,4 dimethyl hexane in the warmed-up products of the hydrogenations of propylene and 1-butene indicated that H atom addition occurs at the terminal carbon and that secondary alkyl radicals are formed. The observed reaction was clean in the sense that complicating processes such as atomic cracking (CH_4 was not observed as a product) did not occur. Hence, if unpaired electron spins were detected, they could be unambiguously attributed to the secondary alkyl radical. As has been mentioned previously, an extensive search using an ESR spectrometer, failed to reveal the presence of these radicals. Consequently, while this technique has provided sound chemical evidence for the formation of a specific radical species, a surprising amount of chemical reactivity reduced the concentration beyond the detectable limits of the sensitive spin resonance technique.

Radical Storage

2.1. Low-Temperature Technique (1° to 100° K)

a. Refrigerants

Inextricably tied to attempts at free radical stabilization is the use of refrigerants for the 1° to 100° K temperature range. The liquids used at NBS are helium, hydrogen, nitrogen, and oxygen with normal boiling points at 4.2°, 20.3°, 77.4°, and 90.2° K, respectively. Lowering the pressure over these boiling liquids makes possible the attainment of temperatures somewhat lower than the normal boiling points. For example, by suitably pumping on liquid nitrogen, temperatures as low as 55° K can be obtained. Similarly a temperature of 1.2° K can be reached by pumping the vapor in equilibrium with liquid helium down to a pressure of several hundred microns.

Liquid hydrogen and helium require somewhat specialized techniques in so far as their storage and transfer from one Dewar to another is concerned. Mr. A. Stober and his several assistants at NBS have not only made these liquids continuously available, but have simplified things for the individual investigator by providing the service of transferring the refrigerant from a storage to the experimental Dewar. In practice, after 24 hours advance notice, at the time designated for an experiment, the refrigerant and an appropriate transfer siphon are brought to the laboratory, the transfer made, and the experiment begun.

b. Dewars

The design of appropriate Dewar systems for the storing of low-boiling liquids has been a necessary activity for most of the investigators in the Free Radicals Research Program. The requirement of minimal heat leak from the surroundings must sometimes be compromised by the types of experiments that are to be performed. The design details of some of the more successful glass Dewars which have been used for optical studies is summarized by Schoen, Kuentzel, and Broida [34]. The metal Dewar used in the electron diffraction studies (fig. 5) is typical of the metal systems constructed at NBS.

2.2. Matrix Isolation

The technique of dispersing molecular fragments in a large excess of an inert solid phase has been extensively studied by Pimentel and his coworkers [35, 36]. These authors conclude that at matrix to radical ratios >100, xenon, argon, and nitrogen provide suitable trapping sites at 20°K and below, while CCl_4, CO_2, and cyclohexane are fairly effective in the neighborhood of the boiling point of nitrogen (77° K). This technique of matrix isolation has been widely used at NBS. Among the most interesting features of the solids containing trapped radicals are the matrix-radical interactions shown by their emission, absorption, and electron spin resonance spectra [7, 12, 17, 37]. Particular attention has been paid to the shifts in energy level from the free gas values, for such species as $N(^2D\rightarrow{}^4S)$ and $O(^1S\rightarrow{}^1D)$ trapped in nitrogen and inert gas matrices. A complete understanding of these phenomena has not been achieved at the time of this writing. However, the wealth of experimental information obtained should stimulate the theorist to address himself to these intriguing problems in solid state physics. A start in this direction has been taken by C. Herzfeld [6, 7] who has shown that a ^2D nitrogen atom interacting with the crystalline field and loosely bound to a neighboring N_2 molecule can qualitatively account for the sharp α lines ($^2D\rightarrow{}^4S$ nitrogen atom transition) observed in glowing, solid nitrogen. A similar treatment [38] for ^1S oxygen atoms trapped in solid nitrogen accounts for the more diffuse β lines ($^1S\rightarrow{}^1D$ oxygen atom transition) which usually accompanies the α group in these emission spectra. The $^2P\rightarrow{}^2D$ transition of atomic nitrogen has also been observed in the near infrared emission spectrum of excited solid nitrogen [12]. A shift of about 40cm^{-1} from the free gas value was observed and satellite lines on either side of the $^2P\rightarrow{}^2D$ and $^2D\rightarrow{}^4S$ transitions are separated from the main lines by about 2,300 cm^{-1}. This value is close to the vibrational frequency of gaseous N_2. Also, the expected isotope shifts have been observed with N^{15}. Thus, the existence of a loose N and N_2 complex is strongly indicated and the interaction between N and N_2 in a solid nitrogen matrix appears to be a mutual one. While these interpretations are by no means final, something like a complete understanding of this system may not be long in coming.

2.3. Stability of Stored Free Radicals

Once it has been established that radicals are present in a cold solid, the question of concentration stability naturally arises. There have been several experiments performed at NBS which have yielded information on this point [28]. Nitrogen atoms (^4S), generated in a solid nitrogen matrix at 4° K by Co^{60} γ-irradiation, were observed with an ESR spectrometer. There was no detectable decrease in signal strength after the solid had been stored at 4° K for 20 hr. Hydrogen atoms (^2S) generated, measured and stored in a similar fashion showed, on the other hand, a distinct decrease($\sim$50 %) in concentration. The γ-irradiation of CH_4 at 4° K resulted in a solid which gave the spin resonance spectra associated with CH_3 and H. After warming this solid to about 20° K and then cooling back to 4° K, it was noted that the ESR signal for H decayed drastically, while the CH_3 signal remained virtually intact. It appears then that hydrogen atoms diffuse and recombine in solid hydrogen and solid methane in the 4° to 20° K temperature range, while CH_3 and N are stable at 4° K in solid methane and nitrogen, respectively. In view of these results, it is not surprising that hydrogen atoms were found to diffuse readily through solid hydrocarbons at 77° K [20]. Livingston and coworkers [39,40] on the other hand, have successfully trapped H atoms in aqueous solid solutions of $HClO_4$, H_2SO_4 and H_3PO_4 at 77° K. This is indeed remarkable in light of the above observations.

An interesting experiment concerned with the stability of ^2D N atoms during evaporation from one cold surface to another has been performed at NBS [41]. The products from a 2,450 Mc electrodeless discharge though nitrogen were collected on a liquid hydrogen cooled surface. The usual glow phenomena associated with the excited solid nitrogen were observed. Another glass surface, downstream from the 20° K one, was maintained at 4° K by liquid helium. When the liquid hydrogen was evaporated, it was found that the condensate formed on the 4° K surface emitted the α lines associated with the $^2D \rightarrow {}^4S$ atomic nitrogen transition. In contrast to this experience are the unsuccessful attempts which have been made at NBS to detect N atoms mass spectrometrically in the gas evaporating from the surface of excited solid nitrogen [42]. Once again it appears that the detection and indentification of radical species requires extreme sensitivity, in this case the ready detectability of the light emitted by ^2D nitrogen atoms.

3. Properties of Stabilized Free Radicals and Free Radical Containing Solids

There have been a number of methods used at NBS for investigation of the properties of solids at low temperatures with and without free radicals present. The types of studies which have been made are characterized in the following list.

1. Spectroscopy (infrared, visible, ultraviolet, and vacuum ultraviolet)
2. Electron spin resonance and magnetic susceptibility
3. Mass spectroscopy
4. Calorimetric studies

5. Measurements on condensed gases at low temperatures
    a. X-ray and electron diffraction
    b. Index of refraction
    c. Thermal conductivity
    d. Dielectric and relaxation measurements.

In addition to the spectroscopic results mentioned previously, some interesting results have been obtained at NBS in the region of the vacuum ultraviolet (> 1200 A) [43]. In this spectral range, scattering is a serious experimental problem. Fortunately, high absorption coefficients are usually encountered so that very thin films can be used, thereby minimizing the scattered light. Solid ammonia, diluted 300 to 1 with argon at 4° K was photolyzed by radiation in 1200 to 2000 A region. Absorption was observed due to NH whose spectral features were similar to those reported by Robinson and McCarty [44] for the products condensed at 4° K from an electrodeless discharge though a 1:25 hydrazine-argon mixture. In addition to NH, absorption due to NH_2 was also observed in the vacuum ultraviolet photolysis of solid ammonia at 4° K. Warmup of the photolyzed NH_3 argon mixture to 35° K showed the disappearance of NH_2 but not the NH. The reason for this behavior is not understood at present. Experiments with the rare gases have shown the resonance lines of xenon (1305 and 1485 A) and krypton (1220 A) can be observed in absorption through thin films of these gases condensed at 4° K. The frequencies at which these lines occur in the solid are only slightly different ($\sim 100 \text{ cm}^{-1}$) from the free atom values, contrary to a recent theoretical prediction [45].

Electron spin resonance [17, 28] and magnetic susceptibility measurements [13, 46] have been employed at NBS to detect, identify and measure free radical concentrations. The radicals examined in this fashion have been N, H, and CH_3 trapped in various solid matrices at 4° K [17, 28], the blue deposit obtained by condensing the dissociation products of HN_3 at 77° K [47], and the various nonequilibrium, colored forms of sulfur which can be frozen at 77° K from the vapor [47]. As a result of these investigations, the unpaired electron spins in the condensed dissociation products of HN_3 [55] are now believed to be due to F-centers in the solid [56], while the various colored forms of sulfur have been shown to be paramagnetic as a result of the presence of unpaired electron spins in polymeric chains of sulfur atoms [57].

In addition to the attempts to detect N atoms evaporating from an excited solid nitrogen surface, mass spectrometry at NBS has been used for such studies as the gaseous recombination kinetics of N atoms [48] and the reaction of N atoms with hydrocarbons in the gas phase [49]. Of particular interest to investigators using the microwave discharge technique has been a determination of the N atom concentration in the afterglow region [48]. This number turns out to be between 1 and 2 percent, thereby providing an upper limit to the concentration of atoms in condensed nitrogen prepared from such a source.

Measurements of the energy liberated by various discharged gases condensed at 4° K have been made [16, 50] at NBS. The results obtained indicate that as much as several percent of trapped energetic species are present in the solids produced in this fashion. These estimates are probably high since the calorimeters used undoubtedly had heat leaks of uncertain magnitude. A precision low temperature calorimeter has been designed at NBS [51] and at the time of this writing, is almost completely built. It is hoped that this device will yield more quantitative values for the energy trapped in solids condensed from gases containing free radicals.

Important contributions in the elucidation of the structure of condensed gases at 4°, 20°, and 77° K have been made by the X-ray diffraction group at NBS. The possibility of obtaining information about the number and type of crystallographic sites available for free radical trapping is an attractive feature of this type of investigation. The materials which have been studied in some detail are argon, N_2, NH_3, H_2O, NH_3, O_2, alcohols, and B_2H_6 [52, 53]. In general, it was found that slow rates of gaseous deposition resulted in solids with a considerably less ordered structure than that obtained during rapid deposition rates. The use of an electric discharge in the gas prior to deposition resulted in increased order in the solid, and when amorphous solids were heated an exothermic annealing to the stable crystalline configuration generally occurred. Certainly part of the released energy observed in the warm up of excited solids must be attributed to these crystallographic changes.

Some interesting results have been obtained at NBS in an electron diffraction study of thin solid nitrogen films at 4° and 20° K [54]. For extremely thin films at 4° K, the observed diffraction patterns indicate the presence of randomly oriented fine crystallites ($<$20 A). As the amount of deposited material is increased, larger crystals are formed which exhibit stacking faults in the direction of the 111 plane. For nitrogen deposited at 20° K, only large crystals ($>$200 A) were observed. Intense electron bombardment of the 4° nitrogen deposit also resulted in a more orderly crystalline structure. In any case, both the X-ray and electron diffraction observations are consistent with the view that more orderly solids are obtained when sufficient energy is available to heat the deposit to a temperature region where annealing of the solid can take place. It seems to be immaterial whether this energy is supplied by the heat of condensation, electric discharge of the gas prior to deposition, or electron bombardment of the solid.

Index of refraction measurements of condensed gases at 4° K have been made [58]. No significant difference in the refractive index was observed when the gases to be condensed were first passed through an electric discharge. This is consistent with the fact that radical concentrations generally do not exceed 0.1 percent. With the ellipsometer used for these measurements it was also possible to make rather precise estimates of film thickness ($\pm$5 A). The application of this technique to the measurement of condensation coefficients would be of great value.

Finally, measurement of the thermal conductivity [59] and dielectric constants [60] of condensed gases have been made. Again, the presence of stabilized radicals was not detected, demonstrating once more the very low concentrations attainable in these cold solids. The intriguing notion of avoiding atom recombination in the solid by depositing a polarized beam of H atoms (the two components being separated in a Stern-Gerlach experiment) has suggested itself to several investigators [61, 62, 63]. However, the results of both theoretical [62] and experimental investigations [61, 63] have not been promising so far.

4. Conclusions

The possibility of stabilizing sizeable concentrations of energetic free radicals now seems quite remote. However, the development of techniques for studying and understanding the behavior of matter in nonequilibrium situations at low temperatures is of unquestioned scientific importance. It is apparent that many incompletely understood phenomena have been uncovered in these investigations. Instead of closing this discussion with a list of NBS accomplishments, the most significant of which have or will appear in the literature, the author prefers to list what he considers the major areas of ignorance. They are:

1. The interaction of condensable gases with low-temperature surfaces (the deposition process).
2. The kinetic details of the chemical processes which can occur in solids below 100° K (low-temperature chemistry).
3. The general problem of the interaction of trapped nonequilibrium species (free radicals being a special case) with its surrounding matrix.
4. The kinetics of the crystallographic changes which have been observed to occur in solids deposited at extremely low temperatures.

and finally

5. The positive identification of some of the free radicals generated by γ-irradiation of organic substances of varying complexity. In particular it would be extremely significant to show whether the present identifications based on the hyperfine structure of ESR spectra are correct.

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WASHINGTON 25, D.C., December 18, 1959.

4. A Survey of Theoretical Work on Trapped Radicals at the National Bureau of Standards

C. M. Herzfeld

1. Introduction

This discussion of the theoretical work done at NBS will be organized on the basis of the qualitative discussion given above as an introduction. In this way we hope to give the best rounded picture of the work, and also to arrive at reliable conclusions about the processes involved. In general, the details of the calculations will not be given here. For these the reader is referred to the published work. We shall concentrate instead on the assumptions, results, and conclusions of the theories.

2. Production and Deposition of Radicals

The first qualitative step is the production of free radicals in the gas phase or in the solid. No theoretical work has been done on this phase of the problem.

The second qualitative step is the condensation of the gas phase onto a solid. It is clear that this process is a very complicated one, and that it has several aspects. The first has to do with the reactions in a flowing gas, and with the composition of the gas just before the impact on the solid. No theoretical work has been done on this.

Rather, all calculations have assumed that a gas of given composition (mole fraction $[R]$ of radical R, mole fraction $[R_2]$ of molecule R_2, and mole fraction $[M]$ of inert molecules or atoms) interacts with the surface. Also nearly all calculations ignore the complex behavior expected of a streaming gas undergoing chemical reactions.

A summary of most of the processes which are important in the deposition is given in table 1. This table is used below to characterize some of the theories. It also gives a graphic indication of the complexity of the problem.

Two types of theories have been constructed to deal with the deposition problem. The first type, essentially statistical, studies the deposition by studying the number of ways in which radicals, molecules and inert species can be laid down together. This is done using various assumptions about the system. In this way upper limits of concentrations of trapped radicals can be estimated, and their dependence on the various parameters of the problem studied. In addition considerable insight into the statistical features of the process can be obtained. The second type of theory studies the detailed mechanisms of the processes involved in deposition. From it qualitative or semiquantitative estimates of "sticking probabilities" can be obtained, as well as insight into the dynamic features of the deposition process.

2.1. Statistical Theories

The first of the statistical theories is due to Jackson and Montroll [1].[1] The theory is based on the following model (i.e., basic assumptions):

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *The processes in the deposition: a schematic summary*

The species: R=atom, free radical

R_2=stable molecule

M=inert atom or molecule

Subscripts: G=gas, S=surface, I=interior of solid

Rate Constants: k_{-i} is the rate constant for the inverse process of constant k_i.

	The Processes	
A. Deposition		
	1. $R_G \to R_S$	k_1
	2. $R_{2G} \to R_{2S}$	k_2
	3. $M_G \to M_S$	k_3
B. Reaction		
	4. $2R_G \to R_{2G}$	k_4
	5. $2R_S \to R_{2S}$	k_5
	6. $2R_I \to R_{2I}$	k_6
C. Diffusion		
	7. R on surface	D_7
	8. R_2 on surface	D_8
	9. M on surface	D_9
	10. R surface→interior	D_{10}
	11. R_2 surface→interior	D_{11}
	12. M surface→interior	D_{12}
	13. R in interior	D_{13}
	14. R_2 in interior	D_{14}
	15. M in interior	D_{15}

One starts with a mixture of R, R_2, and M of known composition in the gas. The gas is deposited in a random way, and each R combines randomly with another R which is a nearest neighbor. Two R which are nearest neighbors are not stable and must combine. All energetic or diffusion effects are ignored.

The problem is thus chiefly a combinatorial one, and concentrates on possible reactions in the solid, once all species are set down in a random manner. This amounts to ignoring processes 1 to 4 and 7 to 15 in table 1, and effectively eliminates competition of various processes.

Three cases are treated in detail. First, the result of depositing a linear chain of R is investigated, and the final concentration $[R]$ in the chain is calculated exactly. This is done by considering all possible configurations of the chain which do not have 2 R in adjacent positions. The result is the following:

$$f=(2x_1+3)^{-1}, \tag{1}$$

where f is the fraction of R in an infinitely long chain, and $x_1=1.3247$ a number which is obtained in the solution of the combinatorial problem. The maximum concentration of R is then given by f, and turns out to be 17.7 percent.

The second case they considered is a one-dimensional chain which contains the species R and M in random positions. An exact solution of this problem is also obtained. The fraction of trapped radicals is given by eq (3.6) of the reference. It predicts a maximum concentration of R of about 19 percent, when the initial beam which is deposited consists of about 45 percent inert atoms. A similar treatment is given for a beam containing R, R_2, and M. Here the R_2 is inert but occupies two lattice sites.

The third case discussed is the three-dimensional condensate obtained, both for the case starting only with R in the gas, and starting with R and M in the gas. This case is solved only approximately. Various lattice types are considered, which differ principally in the number of nearest neighbors of each lattice position. The results are summarized in figure 1. Maximum concentrations of trapped R are seen to lie between 10 and 15 percent. Similar results are obtained when the effect of diluents is considered.

The second statistical theory is due to Golden [2]. Golden considered five different types of situations. They all have the following features in common: The gas is assumed to consist of R, R_2, and M in known proportions. All chemical reaction rates are considered negligibly small compared to k_4 through k_6 of table 1. Recombination is assumed to result from nearest neighbor interactions in the condensed phase. Stabilization is assumed to occur only by isolation of the R by R_2 or M. Diffusion processes are neglected. The problem is treated as a statistical one.

The models considered by Golden are the following:

1. *The Densely Packed Bulk Condensation Model.* This model assumes that all sites in the solid are filled, and each atom or molecule is assumed to take up one site each. Effectively, radicals near each other are assumed to react with one another before they condense. For a given composition of the mixture, the number of ways of arranging this mixture are calculated. The calculation is subjected to the boundary condition that no two R may occupy neighboring sites.

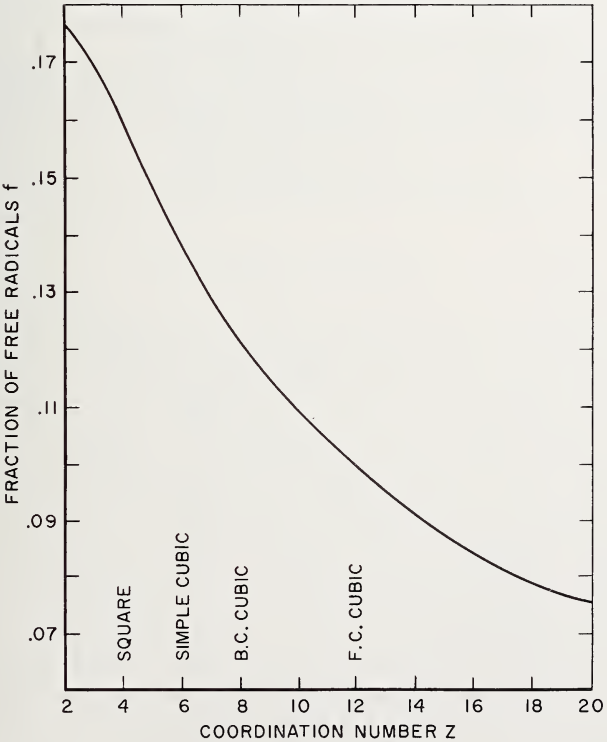

FIGURE 1. *Variation of free-radical concentration with coordinate number z of stabilized matrix.*

(Fig. 6 of Jackson and Montrol [1].)

The calculation also takes into account explicitly the statistical weights of the states of radicals, molecules, and inerts. The results appear as a complicated equation (eq (10) and fig. 5 of [2]) and imply that concentrations of trapped radicals of up to 7 percent may be expected.

2. *The Diffusely Packed Bulk Condensation Model.* In this model it is assumed that all species first condense, one to a site, and then recombine if they can. Vacancies arise from these recombinations. The vacancies are assumed not to contribute to diffusion (which is obviously a doubtful assumption). The results are given in eq (14) and figure 6 of [2], and predict from 3 to over 18 percent of trapped radicals, depending on the number of nearest neighbors and the initial concentration of radicals in the gas.

3. *The Surface Condensation Model.* This model assumes that each condensed layer comes to some statistically stable state before the next layer can deposit. This is a good assumption if the number of collisions of species with the surface is small. Each layer is assumed formed in a way consistent with model 1 above. The results lead one to expect even higher concentrations of trapped radical than model 2.

4. *Nonideal Condensation Model.* This model assumes that species may hit the surface, do not always stick, but evaporate again and react within coming gas in the gas phase. The behavior of this model can be related readily to that of the densely packed bulk condensation model, for which the calculations are given. The results are given in figure 2. As can be seen, the incomplete condensation reduces the percentage of trapped radicals very significantly.

5. *Clustering Model.* Here it is assumed that some clusters of species will be formed in the gas phase, and that the clusters will condense. The model considers that a whole range of sizes of clusters are formed.

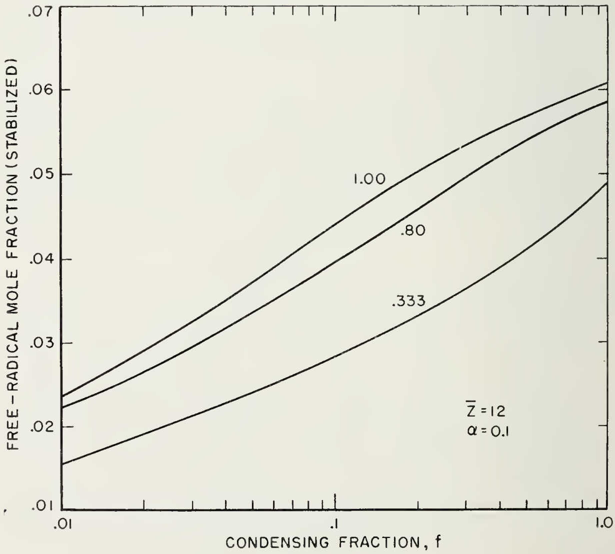

FIGURE 2. *Composition of the densely packed bulk stabilized condensed phase as a function of the condensing fraction f.*

Curves are labeled by mole fraction of free radicals in the gas. (Fig. 9 of Golden [2].)

While the results obtained are not complete, it does not seem that this phenomenon will affect greatly the expected concentration of trapped radicals.

Golden discusses two shortcomings of his treatment. First, nowhere are the energetics of the system introduced into the calculation, and second, diffusion is ignored throughout. It appears to the present author that both features, if taken into account, would lower the expected concentrations of free radicals.

The statistical models of Jackson and Montroll and of Golden have several features in common. They neglect energy considerations and diffusion, hence are likely to give high estimates of trapped radical concentrations. The calculations are of combinatorial type and are either rigorous, or contain sensible mathematical approximations. The various models can be characterized by their assumptions about relative rates of various important processes. This characterization is summarized in table 2. The statistical theories have the advantage of being logically straightforward, but the disadvantage that they ignore important processes, and further that they are not very easy to see through intuitively. The results, however, are clear cut, and are quite useful for the predicting of general trends, if the limitations of the theories are kept firmly in mind.

TABLE 2. *Relations of rate constants assumed by statistical models*

Reference		
[1] Jackson and Montroll	k_1 to $k_3 \gg k_5, k_6$	D_7 to $D_{15} \equiv 0$
[2] Golden	Model 1. $k_4 \gg k_1, k_5, k_6$	D_7 to $D_{15} \equiv 0$
	Model 2. k_1 to $k_3 \gg k_5, k_6$	D_7 to $D_{15} \equiv 0$
	Model 3. k_1 to $k_3 \ll k_5, k_6 \ll k_4$	D_7 to $D_{15} \equiv 0$
	Model 4. $k_1 \approx k_4$ to k_6	D_7 to $D_{15} \equiv 0$
	Model 5. Same as model 1, with clustering	D_7 to $D_{15} \equiv 0$

2.2. Kinetic Theories

The only attempt so far at a discussion of the details of the process of deposition has been carried out by Zwanzig [3]. He attempts to calculate the probability of adsorption of an atom on a solid. He chooses a very simple model: The solid is represented by a semi-infinite chain of atoms connected by nearest neighbor interactions. The lattice is initially at rest (effectively: $T=0$°K), and the energy transfer is calculated for a collision of an atom with this chain at rest. The precise point is the following: In previous theories of this phenomenon it has seemed that it is difficult for an atom to transfer appreciable amounts of energy to the chain. Certain approximate quantum mechanical calculations had indicated that processes in which the lattice absorbs more than one phonon are unlikely. This would mean a low-sticking probability, i.e., the atom would hit and nearly always rebound again. Zwanzig has examined this feature with considerable care. He calculates the critical kinetic energy of the incoming atom, i.e., that kinetic energy above which the particle is always reflected. It turns out that this critical kinetic energy depends strongly on the ratio μ=mass of incoming atom/mass of atom in chain. Exact solutions can be given for $\mu=1$ and $\frac{1}{2}$, and a good asymptotic solution for small μ. The mass effect is important. For $\mu=1$ large *amounts* of energy are transferred effectively. (This corresponds to the many-phonon prosesses, which were previously thought to be unimportant.) For $\mu < 1$ less energy is transferred. The largest *fraction* of the energy is transferred when the original energy is low.

It is clear that this theory has several limitations. The most serious are the one-dimensional model of the solid, and the classical treatment of forces. In spite of these the theory should predict the mass effect reasonably well. A higher (2- or 3-) dimensional solid will make transfer of energy easier, but probably not change the qualitative features, and only for hydrogen are the quantum effects likely to dominate. The theory should be particularly good for the prediction of relative deposition rates of various noble gases on crystals of noble gases.

3. Emission and Absorption of Energy

When the mixture of gas containing R, R_2, and M condenses, radiation is sometimes emitted. This arises either because excited species are deposited, which radiate during or after deposition, or because species react, such as $2R \rightarrow R_2$, and produce highly excited new species. When the deposit "settles down" one can often observe absorption of energy. Three broad theoretical problems have been investigated. First, historically, the emission of radiation from nitrogen deposits has attracted considerable effort. Second, the paramagnetic resonance absorption of hydrogen deposits has been studied. And third, the effects of the solid on the absorption spectra of molecules have been investigated. We shall take up each of these broad inquiries, and see what conclusions they have led to.

3.1. Emission of Radiation from Nitrogen Deposits

Very early in this work, before the Free Radicals Program was initiated, a semiquantitative interpretation of some features of the very complex light emission from nitrogen deposits was given by Herzfeld and Broida [4]. The general point of view was adopted that in the deposition of nitrogen which has passed through an electric discharge, N atoms are deposited, these radiate, and then recombine giving excited N_2 molecules which also radiate. In this manner the α lines were interpreted as arising from the highly forbidden transition $^2D \rightarrow {}^4S$ in N atoms, the β lines were ascribed to transition between high-lying levels in N atoms, and the A-bands were assigned to the transition $^5\Sigma$ to $^3\Sigma$ of newly formed N_2 molecules. The arguments were qualitative. It is now clear that the α lines do indeed arise from a transition like that proposed, though the situation is known to be vastly more complex than thought at the time. The β lines and A-bands belong to transitions of oxygen atoms and molecules, respectively.

Later an attempt was made by Herzfeld to analyze the structure of the α-lines in detail [5]. He applied crystal field theory to the analysis of the spectrum. As before, the α lines are assumed to arise from the transition $^2D \rightarrow {}^4S$. The effects of the solid on the positions of the levels appear through off-diagonal matrix elements of the crystal field, while the transition probabilities are affected by a combination of crystal field and spin-orbit coupling. (See figure 3.) By assuming the values of two crystal field parameters, and of one atomic parameter, the positions of all five spectral lines of the α group which were known then

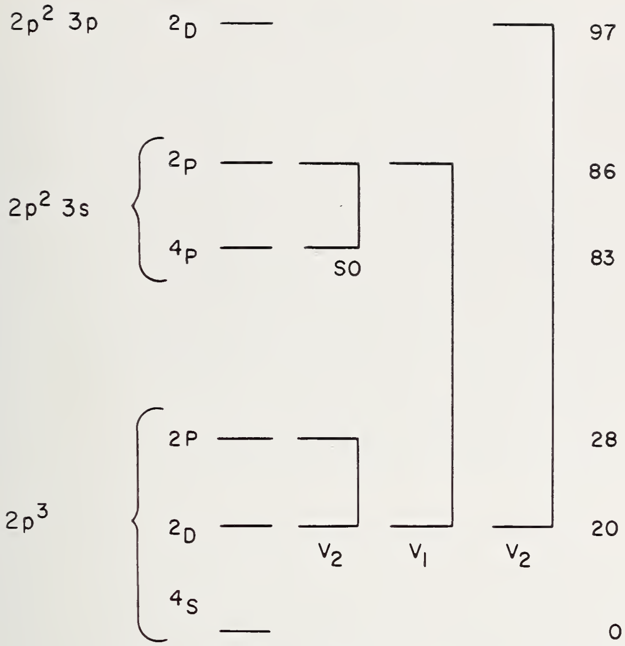

FIGURE 3. *Schematic summary of levels involved in the α-line spectrum.*

SO represents mixing through spin-orbit coupling; V_1 through linear potential terms; V_2 through quadratic potential terms. Numbers on the right give energy in units of 1,000 cm^{-1}. (Fig. 2 of Herzfeld [5].)

were fitted quite well. (See figure 4.) Also relative transition probabilities were predicted which agreed well with the measured relative intensities. A numerical model was constructed to relate the crystal field parameters needed to fit the data to the geometry of the trapped N atom. Because of the short range forces in solid N_2, and because of the low symmetry of the trapping site required to fit the data, it was argued that each N atom was perturbed by, and attached loosely to, one N_2 molecule only. On the basis of a point charge model some estimates of the configuration were given. The theory had one major intrinsic flaw. To obtain agreement between calculated and observed energy levels, a wholly unreasonable value of η, the spin-other-orbit coupling constant of the trapped atom had to be assumed.

It is now known that the details of this analysis are wrong. First of all, eight or perhaps more lines have been observed in the α group. This implies [5] that more than one trapping site is available to the N atoms. Second, the intensities have been shown to be very poor indicators of the transition probabilities. When they are compared [6] with measured half-lives, they prove without a doubt that there exist wide variations in the populations of the excited states. The general ideas of the theory continue to be applicable, as shown by the analyses of spectra discussed in the preceding paper, but the details of the calculations must be modified.

In the deposition of "excited" nitrogen gas, some oxygen is apparently present. It has been shown (see the preceding paper) that the β lines observed in nitrogen deposits arise from transitions in trapped oxygen atoms. Goldberg and Herzfeld [7] have applied a crystal field analysis to the proposed transition, namely $^1S \rightarrow {}^1D$, and have found

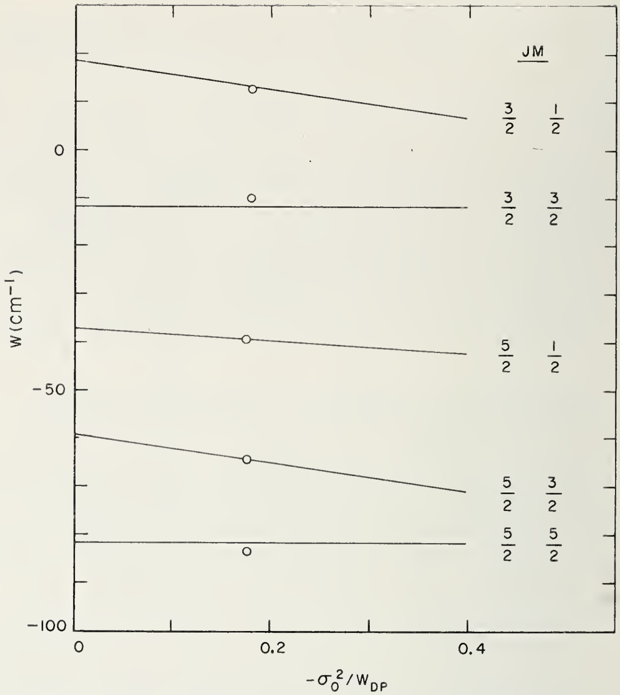

FIGURE 4. *Comparison of theoretical energy levels with early observed levels for the α-lines.*

The theoretical levels are plotted versus $-\sigma^2/W$ for $|\sigma_2|=230$ cm^{-1}, and $\eta=3.46$ cm^{-1}. Circles indicate experimental values. Newer data are yet to be interpreted. (Fig. 3 of Herzfeld [5].)

reasonable agreement between experiment and theory. Again it is assumed that each O atom which radiates is held in loose complex with one N_2 molecule. Similar techniques have been applied to the ground-state, ^3P, of trapped O atoms. This calculation has shown that the electronic ground state of trapped O atoms is very likely nondegenerate, and that the next higher level lies several cm^{-1} above the ground state. This result explains the absence of paramagnetic resonance absorption by trapped O atoms.

Recently Griffing has investigated the α lines from a different point of view [8]. She assumes that an N atom replaces an N_2 molecule in the lattice, and then moves to readjust the lattice in such a way as to minimize its energy. Several nonequivalent motions of this type can be found, which give rise to enough levels to explain the α group. So far the results obtained are only qualitative, but the approach is a very promising one and is complementary to crystal field theory.

3.2. Paramagnetic Resonance Absorption

When atoms with an odd number of electrons are trapped in a solid, they are very likely to exhibit paramagnetic resonance absorption. Griffing, Jackson, and Ransil [9] have examined in detail the theoretical paramagnetic resonance absorption spectrum of the molecule H_3. Their motive was to see what this spectrum would look like, to make an experimental search for this molecule easier. Also, at about the same time, the resonance absorption of hydrogen deposits was being studied by Jen, Foner, et al. at the Applied Physics Laboratory. They observed, among many other spectra which they interpreted, a spectrum which defied interpretation at the time, and which was conjectured by some to arise from H_3. (The spectrum has since been interpreted by Jen and Foner as being due to the radical SiH_3.)

The method of calculation was the following: First, the best wave functions for a linear H_3 molecule with equidistant H atoms were calculated. This was done in the LCAO-MO-SCF-CI scheme. (This means that Linear Combinations of Atomic Orbitals were used to construct Molecular Orbitals, that a set of these molecular orbitals was picked which give a Self-Consistent Field for each electron to move in, and that Configuration Interaction was taken into account to some extent. For details of the method the reader is referred to the reference, and the literature cited there.) Second, once the best functions, and the total energy, were available, these functions were used to calculate the hyperfine coupling constants, i.e., the magnitude of the interactions of the electrons with the magnetic moments of the nuclei. Last, the energy levels of the molecule in an external magnetic field are calculated.

In the first part of the calculation, the effective atomic number Z of the atomic wave functions, and the equilibrium separation R_{ab} of the atoms are varied, until the lowest value of the energy of the molecule is found. $Z=1.10$ and $R_{ab}=1.90$ atomic units give the lowest energy. In the second part, the Fermi interaction between the electrons and the nuclear magnetic moments was calculated. The dipole-dipole magnetic interaction between the electrons and the nuclei was ignored, because it was shown to be smaller than the contact interaction. Third, the energy of the molecule in the external magnetic field was obtained with second-order perturbation theory. The energy levels in the absence of this field were also calculated.

The results of the calculation are the following: The calculated total energy was correct to about 4 percent, the calculated binding energy was 65 percent of the correct value. The predicted resonance spectrum is quite different from any that have been observed so far. It consists of two doublets near the free electron resonance, and two more doublets, one on each side of the free electron resonance, very far away from it. (This separation of the two far doublets is greater than the H hyperfine splitting.) The spacing of the central doublets is quite sensitive to the contribution of configuration interaction to the wave function. This part of the spectrum is shown in figure 5.

A calculation of the resonance spectrum of H_2^+ was also carried out for comparison.

The conclusion of the calculation was that no H_3 had been observed so far.

The only other discussion of resonance absorption carried out in the NBS program is that of Goldberg and Herzfeld for trapped O atoms, which was discussed above [7].

3.3. Molecular Spectra of Trapped Species

The effect of the solid on the spectra of molecules has been investigated by Zwanzig [10]. He has treated two problems. First, the shift and broadening of the spectrum of a molecule in a lattice composed of the same molecules, and second, the shift of the spectrum of a molecule in a lattice of inert atoms.

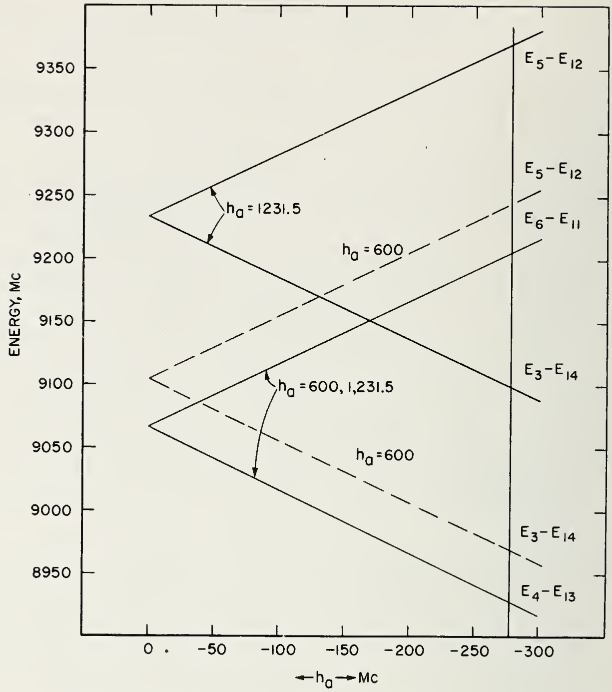

FIGURE 5. *Theoretical spectrum for* H_3, *as a function of two hyperfine parameters,* h_a *and* h_b.

Only the four central lines are shown. The solid lines belong to the calculated value of h_a=1,231 Mc, h_b=−227.2 Mc. (Fig. 1 of [9].)

The first calculation is based on the interaction of the dispersion dipoles of the molecules. (A molecule may have a momentary dipole due to fluctuations in its electron distribution, this dipole induces a dipole in a neighbor, these dipoles interact, and so forth.) The various moments of the spectrum are calculated. The zeroth moment gives the total absorption, and is not affected by the interaction. The first moment gives a small shift, due to electrostatic perturbations. The second moment gives the widths of the lines, it arises from fluctuations in the total potential which are due to phonons or imperfections. A numerical estimate of line width for anthracene crystals gives the correct order of magnitude.

The second problem arose from an observed slight shift in the Vegard-Kaplan system of the emission spectrum of N_2 trapped in argon. Zwanzig estimates the shift in the ground state of N_2 in argon. Three approaches are investigated. Simple dispersion theory is used with the polarizibility of solid argon calculated from the index of refraction, and interactions between N_2 and A calculated from Lennard-Jones potentials. The result depends on the frequencies for the N_2 vibration, hence on the vibrational quantum number of N_2. This calculation gives the correct magnitude (approximately 5 cm^{-1}) and direction (to the red) of the shift. Two other effects were studied, both gave results several orders of magnitude too small. They were the force arising from quadrupole-induced-dipole interactions, and second order dispersion theory.

In summary, a fairly large amount of work has been done on the theory of the spectra. This work has shown beyond doubt that some phenomena are explained in a simple and straightforward way by assuming that active species are trapped in the solid. Furthermore, this work has solved a large number of special problems. The precise nature of the solutions will undoubtedly change as more details are observed, but the general picture seems very firmly established.

4. Trapping Forces and Structures

A number of significant facts about trapping forces have been discovered in the work under consideration. It has become fairly clear that the trapping of atoms in molecular lattices is a quite complex phenomenon. It is evident that loose complex formation with molecules occurs often, at least in the case of N trapped in N_2 and O trapped in N_2. The theoretical evidence was discussed above, but the most striking evidence comes from experiment, particularly from the α' and β' line groups.

Another method to investigate trapping forces has been used by Jackson and Castle [12]. They investigated the following question: Are there any positions in or on an N_2 lattice where an N_3 molecule could rotate, either freely or in a hindered manner? Experimental evidence for such behavior exists, in portions of the α'' group of spectral lines. Jackson and Castle calculated the energy levels of molecules on the surface of the crystal, and also studied the long-range interaction potential between N and N_2. So far their results are inconclusive.

As pointed out above, crystal field theory has been a useful tool in the interpretation of spectra of trapped radicals. The theory has, however, the basic flaw that it is difficult to correlate the "fitted" values of the parameters of the theory with geometrical models. An attempt has therefore been made [13] to investigate the nature of crystal field theory itself, using essentially molecular orbital techniques. The model studied consists of an excited H atom (in a $2p$ state) and an unexcited H_2 molecule. The interaction energy is calculated in two ways. First a modified molecular orbital type treatment is used, then a crystal field type, and the two compared. The procedure sheds considerable light on crystal field theory, and may provide a good (though complicated) calculational scheme for the crystal field parameters.

Calculations of properties of two triatomic systems are being done by Boyd [14]. The method is molecular orbital theory in both cases (LCAO-MO-SCF-CI method). One molecule studied is linear N_3 with equidistant N atoms. The range of ρ (interatomic distance between 2 N atoms) is $r_0<\rho<2r_0$, where r_0 is the interatomic distance for the N_2 groundstate. The second molecule being studied is HO_2. The geometry is that of a right triangle, with assumed $r(\text{O—H})$ as in H_2O and $r(\text{O—O}) \approx 1.3$ A, which is typical for superoxides. These calculations should give a qualitative or semiquantitative idea of such things as binding energies, energy of excited electronic states, and of energy as function of geometry. From these a rough idea of the spectra can be obtained.

In another investigation, Boyd has collaborated [15] in working out some crystal structures from X-ray diffraction. These studies centered on establishing the structure of the α phase of N_2 (which is stable at low temperatures). There has been some controversy about this structure in the past. The present work established the space group of the α phase as *Pa*3, thus showing that Vegard's early result was incorrect. Furthermore, electron density maps were prepared [16] of the α phase. Several questions still remain unsettled in this problem such as precise N—N distances.

5. Thermodynamics of Radicals

It is of interest to inquire whether radicals exhibit unusual thermodynamic properties, either when free or trapped. Clearly, in a system in equilibrium the concentration of free radicals can be calculated from thermodynamic data. For light radicals of the type under consideration here, it is obvious that at equilibrium at low temperatures the concentation of such radicals will be minute. The point is, however, that it may be possible to prevent the system from coming to equilibrium, and thus amounts of radicals larger than equilibrium may be kept for some time. This was the philosophy of the statistical trapping papers of section 3. A quite different approach was the attempt by Jackson and Pollack [17] to investigate the equation of state of H atoms. Of course the H atoms would normally recombine, but if they could be kept from doing so, say, by collecting atoms in a very strong external magnetic field with their spins parallel, then they will recombine only at some slow rate (yet unknown) and there is a real point in discussing the thermodynamics of such an assembly. They apply de Boer's theory [18] of condensed permanent gases (which is a type of corresponding states theory) to H, D, and T atoms, which are assumed to be kept in parallel spin states. From a minimum of experimental data they obtain energies, densities, and critical temperatures for liquids supposed formed from these atoms. The application of the theory to these atoms is not fully worked out. If some means can be found to collect spin oriented atoms, this method for predicting their properties may become useful.

6. Disappearance of Trapped Radicals

From qualitative observations it is obvious that trapped radicals disappear by at least two distinct mechanisms. These observations are most clear-cut in the case of nitrogen deposits. Here one has known from direct observation from the earliest experiments, that several types of flashes occur during deposition or during warmup. One type of flash seems to propagate so rapidly that it appears to cover an area of several square millimeters instantaneously. A second type of flash propagates slowly enough that the movement of a definite front can be discerned. This has been called by many a cold flame. Recent thermal and magnetic studies by Fontana (see the previous paper for reference) indicate these flashes seem to be intimately connected with some critical concentration of trapped radicals. This has led Jackson [19] to work out an elegant treatment of stability in trapped radical systems, and of the ways in which unstable systems disappear. Recently Reed and Herzfeld [20] have given a treatment of the speed of the slowly moving "flame". Thus two aspects of the disappearance of trapped radicals can now be understood.

Jackson's work consists of three major parts. The first part uses qualitative arguments to obtain a simple expression for a critical concentration, n_c, of trapped radicals, which, if exceeded, gives unstable systems which decay explosively. The second part consists of a detailed analysis of discrete sequences of radical reactions, with an analysis of the circumstances under which steady states can exist. The third part involves a study of the partial differential equations for the average values of concentrations. Remarkably, all three treatments give the same criterion for stability.

The first, qualitative, theory goes as follows. One assumes: (1) A lattice of R_2, with R distributed at random; (2) the R are in traps, sufficiently deep that at 4° K no diffusion of R takes place; and (3) all traps are assumed alike, with a given trapping energy W_T. Now, when $2R \rightarrow R_2$ the released energy is assumed to heat a volume V of the lattice, and to free the R in this volume. The probability that an R so freed combines with another R is estimated, and it is assumed that this probability is zero except near the place where the R comes to rest again. If the average number of secondary recombinations is equal to one, i.e., if every R produced in a recombination itself recombines itself again, a steady state exists. This gives the following equation for the critical concentration:

$$\frac{n_c}{M} \approx 0.79 \times 2.36 \sqrt{\frac{\alpha k(T_f - T_0)}{\zeta W}},$$

where n_c is the critical concentration of R, M the concentration of R_2, α a number of order unity chosen to give a reasonable average specific heat of the solid, k the Boltzman constant, T_f the threshold temperature for release of radicals, T_0 the initial temperature of the deposit, ζ is related to the probability of capture of an R, and is of the order of the coordination number of the R in the lattice, and W is the energy released in each recombination. If one assumes reasonable values for the parameters one obtains $n_c \approx 0.7$ percent. A maximum estimate (straining all plausibility) gives $n_c \approx 4.7$ percent, a similarly unlikely minimum estimate gives $n_c \approx 0.2$ percent. This qualitative theory has a number of obvious flaws. It treats the heat release macroscopically, all else microscopically. Further, all the released energy does not go into the lattice, some is radiated. Also, the estimated probability of recombination may be too low. None of these are likely to affect the final result greatly, except that the low estimate of the recombination probability leads to a predicted value of n_c which is too high. Several important conclusions can be drawn from this qualitative theory directly. First, and most important, the maximum concentrations of trapped R likely to be stable are about 1 percent. Second, there is little point to cool the lattice much below 4° K. Third, the value of n_c does not depend greatly on the substance used.

The second approach used by Jackson is a detailed analysis of the structure of radical chain, and its dependence on the parameters of the problem. In particular the probability of terminating chains is studied. It can be shown that when $n < n_c$ all chains terminate, and the system as a whole is stable. When $n = n_c$, nonterminating chains exist, which lead to explosions. The expression for n_c obtained is the same as above.

The third method involves writing down partial differential equations for the averages of the variables. These equations give the same criterion for stability which was obtained before.

Several special calculations are carried out by Jackson. The concentration of R in an irradiated solid is calculated as a function of time, and a saturation curve obtained (see fig. 6). This should describe irradiation experiments quite well. Another special calculation gives the effect of size on stability. As in nuclear pile theory, the smaller the sample, the larger the stable concentration, because then some radicals escape without producing secondaries. Finally, another value of $n_c=0.13$ percent was obtained from the theory using late experiments.

Reed and Herzfeld [20] have given a semiquantitive theory of the speed of a diffusion controlled slow flame through the deposit containing trapped N atoms. These slow flashes have a speed of propagation of approximately 2 cm/sec. The theory is simple. The flame front heats up the material ahead of it, releases trapped R which recombine, this heats up material ahead of them, and so forth. Simple calculations using fairly reasonable approximations show that the speed of propagation v of the flame is of the form

$$v=(2e^{-2}\ln 2)^{\frac{1}{2}}\ (K\nu n)^{\frac{1}{2}} \qquad n=\text{mole fraction of radicals},$$

where K is the thermal diffusivity of the solid N_2, and ν is a frequency characteristic of the jumping rate of species in the lattice, and hence related to the diffusion rate. Using a measured value [21] of K, and an upper limit of ν obtained from the width of the hyperfine lines of N atoms in paramagnetic resonance absorption, an upper limit of v of 3 cm/sec is obtained. This agrees very well with the observed speed, considering the crudeness of the theory.

These theories account satisfactorily for different aspects of the disappearance of radicals, but the relation between the two theories is not clear.

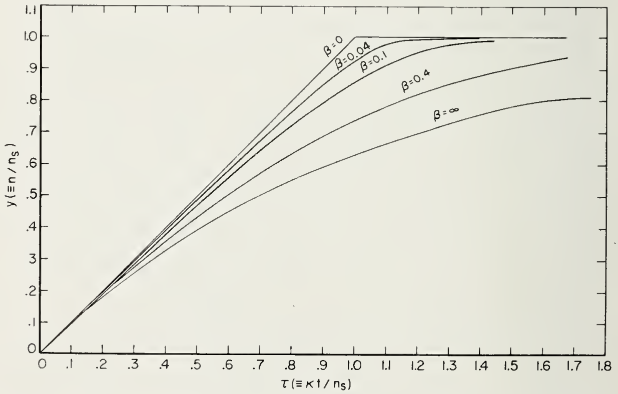

FIGURE 6. *Theoretical radical concentration* n *as a function of time* t *in an irradiation experiment.*

n_s is the saturation concentration, K the number of R produced per cubic centimeter per second and $\beta=\zeta n_c/M$. (Fig. 2 of Jackson [19].)

7. Conclusion

We shall attempt to summarize here both the results and the remaining problems. While much has been accomplished, it is probably true to say that there are now more questions than there were three years ago, and more questions now than there are answers. Of course, many special results have been obtained; these have been discussed in the preceding pages. But, more importantly, the theoretical work was usually done in close contact with the experimental work, has stimulated it and was stimulated by it. In this way it has had indirect effects which are impossible to demonstrate, but which are quite evident to the members of the Program.

Several new fields have been opened up or significantly expanded. To this writer the most important seem to be two: (1) The theory of chemical condensation, of condensation of chemically reacting gases. This field is of unusual complexity because of the interactions of chemical, solid state, hydrodynamic, and statistical effects. The field has considerable importance in many scientific and engineering applications. Only a beginning has been made, mainly on the statistical parts of the problem. (2) The theory of photochemistry of solids. Much experimental work has been done elsewhere, and some theory also, but in the efforts described above one can discern the beginnings of systematic theoretical approaches to the interaction between photochemical and solid state effects.

A field in which existing theoretical techniques have been applied to new systems and circumstances is the theory of spectra of solids. While few new theoretical ideas have emerged from this, the range of applicability of existing theories has been extended significantly.

What are some of the outstanding problems which still require attention? Perhaps the most important of these is the very fundamental one of describing in detail the interactions between two reacting species. This is a venerable, unsolved problem of chemical physics and a good deal of thought goes into it these days. Here the problem would be modified by the presence of solid state effects.

The two new fields of "chemical condensation" and "photochemistry of solids" need considerable theoretical development before they can be said to be established.

Furthermore a host of special problems need attention, such as interpretation of spectra, calculation of energy levels of unusual species, and so forth.

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WASHINGTON, October 14, 1959.

5. Low-Temperature Chemistry

Ralph Klein[1]

1. Introduction

The interest in free radical stabilization in recent years has stimulated investigation of chemical reactions at low temperatures and emphasized that because of the many unique problems and techniques low-temperature chemistry can be considered a distinct discipline. This review of low-temperature chemistry will be limited to chemical reactions that occur at temperatures below 150° K, an arbitrary upper temperature limit. No attempt has been made to be exhaustive; the major emphasis has been on work done within the National Bureau of Standards Free Radicals Research Program.

Whether a chemical reaction can occur at a given temperature at a conveniently measurable rate depends, among other things, on the activation energy through the Arrhenius relationship. It is quite evident that low-temperature chemical reactions will be characterized by low-activation energies, in general less than 5 kcal. This encompasses radical-molecule, radical-radical, ion-molecule, ion-ion, certain molecule-molecule reactions, and some catalytic reactions. Usually these will be reactions occurring either in the crystalline or the glassy state, although the liquid and gaseous states are not excluded. In distinction to the high temperature regions, problems of diffusion, both thermal and particulate, assume great importance. Chemical reactions become simpler since secondary reactions are usually absent. Although the number of reactions that can be investigated is limited, the development and application of optical spectroscopy, electron spin resonance, field emission microscopy, and other techniques to the low temperature region, have greatly increased the scope within which an understanding of low-temperature reactivity can be developed.

The preparation of systems capable of reacting at low temperatures, and the control and measurement of parameters such as temperature, rates, and concentration often present formidable experimental difficulties. Experiments with radical reactions require preliminary preparation such as high-temperature pyrolysis or electric discharge followed by a rapid, low-temperature condensation. Other methods include photolysis, γ-irradiation, X-ray, electron, ion, or free radical bombardment of solids. Many of these techniques have been used successfully, often with interesting results.

The series of investigations of Geib and Harteck in 1932 and 1933 [1, 2, 3][2] were among the first in low-temperature chemistry. Their experiments consisted in mixing a gas that had passed through a glow discharge, and hence contained free radical species, with another gas in a reaction vessel at liquid air temperature. Condensable products, if formed, froze out on the walls and could be subsequently analyzed by conventional methods after warmup. In this way they observed that atomic hydrogen reacted with oxygen, nitric oxide, sulfur dioxide, ethylene, and benzene. They reported what they considered to be a

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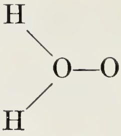
[1] Guest scientist from Olin-Mathieson Chemical Co., New Haven, Conn., now NBS staff.

[2] Figures in brackets indicate the literature references at the end of this paper.

new form of hydrogen peroxide, , from the results of their experiments with H atoms and molecular oxygen.

2. Rapid Condensation of Reacting Gases

Ruehrwein, Edwards, and Hashman [4, 5, 6] in recent articles, have refined the technique of Geib and Harteck in that the gases could be condensed at liquid helium temperature. Their reaction vessel is shown in figure 1. Edwards and Hashman [6] investigated the reaction of H atoms with oxygen, condensing the reaction products on a liquid helium cooled surface. A solid was obtained which evolved oxygen at about 160° K and left a residue of water and hydrogen peroxide when finally warmed to room temperature. Similar results were obtained when the experiments were done either with water discharge products or H atoms with ozone at 77° K. It appeared that the oxygen evolving solid was a gel-like molecular complex of O_2 and H_2O_2 and/or H_2O. A solid of similar characteristics could be prepared by condensing oxygen with hydrogen peroxide at 4.2° K. The radicals HO_2 and the hypothetical H_2O_3 and H_2O_4 were not involved to any appreciable extent, nor was it necessary to invoke any structurally new species, according to these authors.

The interpretation of the Geib-Harteck experiments, as extended by Ruehrwein, Edwards, and Hashman, is uncertain in some respects. The temperature and physical state under which the free radicals produced in the discharge tube react are not defined. There are several nonmutually-exclusive possibilities: (1) reaction in the gas phase; (2) reaction in the solid during deposition; (3) reaction in the solid during warmup. It seems probable, however, that at least part of the reaction occurs at temperatures well below 150° K.

Ruehrwein and Hashman [5] studied the formation of ozone from atomic oxygen at low temperatures. The deposit of discharged oxygen condensed on a 4.2° K surface was initially faint blue. The color became more intense upon warming through the temperature range 13° to 30° K. As noted, this is not necessarily an indication of chemical reaction in the solid. Oxygen undergoes a phase transition at 23.7° K, and this may account for the change in appearance of the deposit. Indeed, Harvey and Bass [7], showed that the concentration of ozone present in the solid as deposited showed no increase on warming.

Ruehrwein, Hashman, and Edwards [5] examined the products of several gases that had been passed through a discharge and condensed at 4.2° K. Table 1 is a summary of the results. They also found that molecular oxygen forms complexes with several solids such as hydrogen peroxide, water, and nitrogen dioxide. These complexes appear to be stable at the boiling point of oxygen.

Free radicals may be prepared by thermal decomposition reactions. Rice and coworkers [8, 9] have carried out several interesting experiments in which gases, after being pyrolyzed at high temperatures, were rapidly condensed on liquid nitrogen cooled surfaces. Chemical reaction could often be observed in these frozen solids well below 150° K

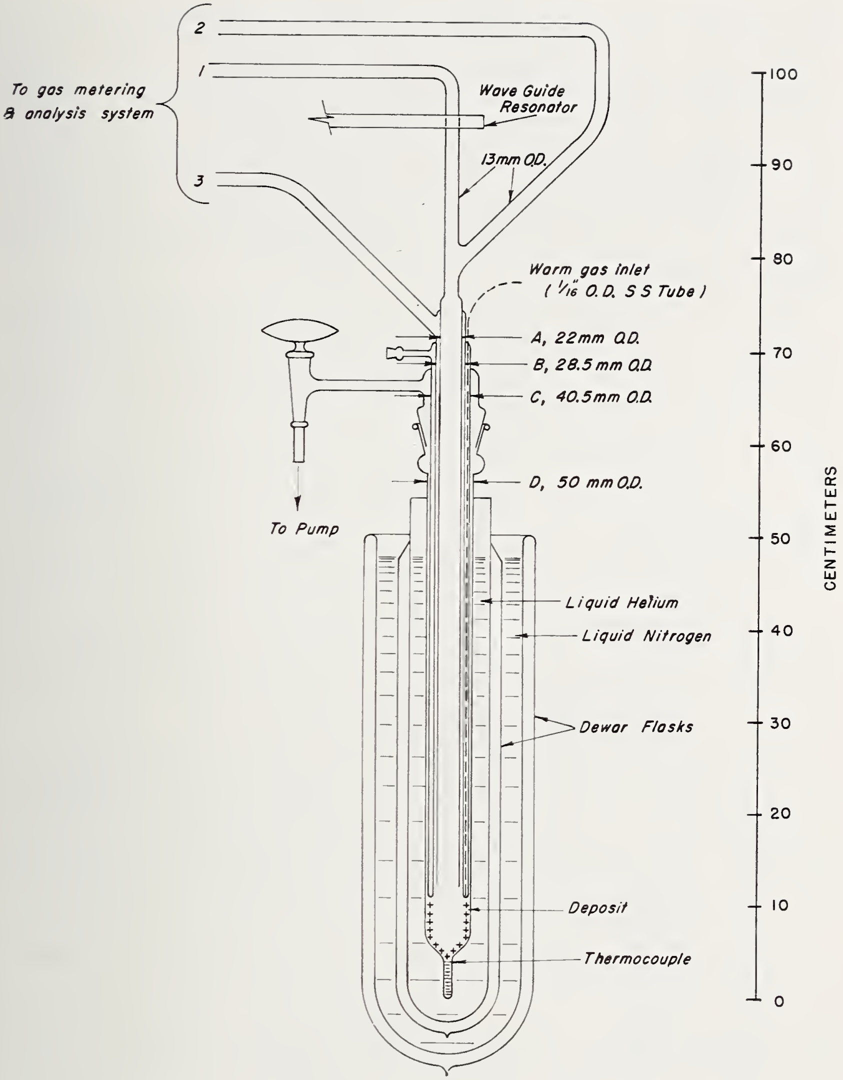


Figure 1. *Reaction vessel for investigation of reactions involving free radicals at low temperatures.*

Table 1. *Observed products from discharged gases after condensation and evaporation*

Gas discharged	Principal stable products
O_2	O_3
H_2O	H_2O_2, H_2
NO_2	N_2, O_3
NH_3	N_2, H_2
CO	C, CO_2
CO_2	CO, O_3
SO_2	O_2, S

For example, Rice and Scherber [8] passed hydrazine through a furnace at 850° C and condensed the products on a liquid nitrogen cooled finger. The condensed material was yellow in color. It decomposed exothermally with disappearance of the color at −178° C to give N_2. Rice and Grelecki [9] observed that the green solid, condensed at −196° C from the products of discharged dimethylamine, became lighter on standing. Since a temperature dependent H_2 evolution accompanied the process, they were able to measure an activation energy for the process of 1.3 kcal. It was assumed, as in similar experiments, that free radical species in the solid react to give the observed products.

Films of condensed pyrolysis products of azo-ethane are being studied by Comeford [10] at the National Bureau of Standards. Azo-ethane (plus argon as a diluent) is passed through a furnace in the region 200° to 500° C. The products are condensed on a 4.2° K cesium iodide window 1 to 2 cm distant from the exit of the furnace. Figure 2 shows the experimental arrangement. [11] Infrared spectra of the films formed under various flow and temperature conditions are recorded. The gases from the film after warmup are collected and analyzed with a mass spectrometer. Ethane, ethylene, butane, and methane have been identified both by infrared and mass spectrometric analysis. From indications that under some conditions the amount of butane in the products, as determined by mass spectrometry of the gas phase, had increased over that found by infrared analysis of the condensed gases at 4.2° K, it may be inferred that ethyl radicals were stabilized in the condensed phase. Unambiguous evidence of reaction in the solid from differences in the infrared spectra as the film is warmed above 4.2° K has not as yet been obtained.

Kuentzel [12], also employing the apparatus as shown in figure 2, has been studying the ethylene oxide pyrolysis products condensed on a 4.2° surface. Infrared spectral features differing from that of ethylene oxide or other possible stable reaction products have been observed. The intensity of these features is stronger the shorter the distance between the furnace exit and the condensing surface.

3. Atomic Beam Deposition and Surface Processes

In an attempt to stabilize iodine atoms, Scheer [13] condensed an iodine atom beam on a nitrogen cooled Pyrex glass surface figure 3. The condensed iodine was observed by measuring the intensity of the I_2 absorption bands during buildup of the deposit. No difference could be detected between the condensed film formed by an atomic iodine beam and that of a molecular beam on a per-number basis. This is shown in figure 4. It was estimated that for a pure I_2 deposit, a change in absorption corresponding to a 3 percent difference in film thickness would be detectable. Even when *n*-heptane was made to impinge on the condensing surface with the iodine in a ratio of 250 to 1, no change of the deposit of the iodine atom beam from that of the molecular beam was observed. Since the iodine atom recombination in the solid must be diffusion controlled, sufficient mobility for atom-atom encounters must occur during the deposition process, for once the beam is deposited, no boundary spreading of the condensed spot can be detected even after several hours.

Surface diffusion processes may be examined in some detail with the

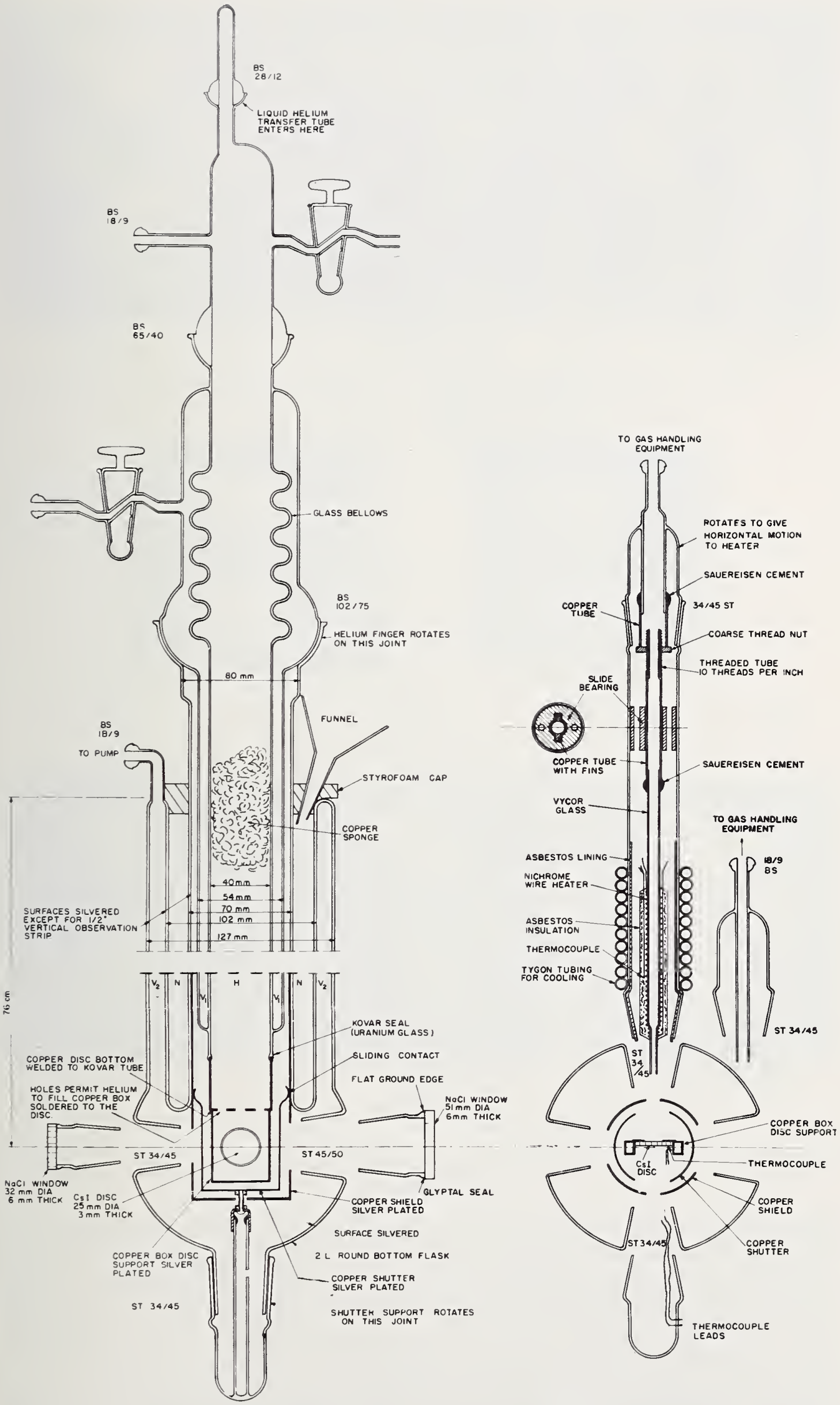


FIGURE 2. *Apparatus for the study of pyrolysis products condensed rapidly at low temperatures.*

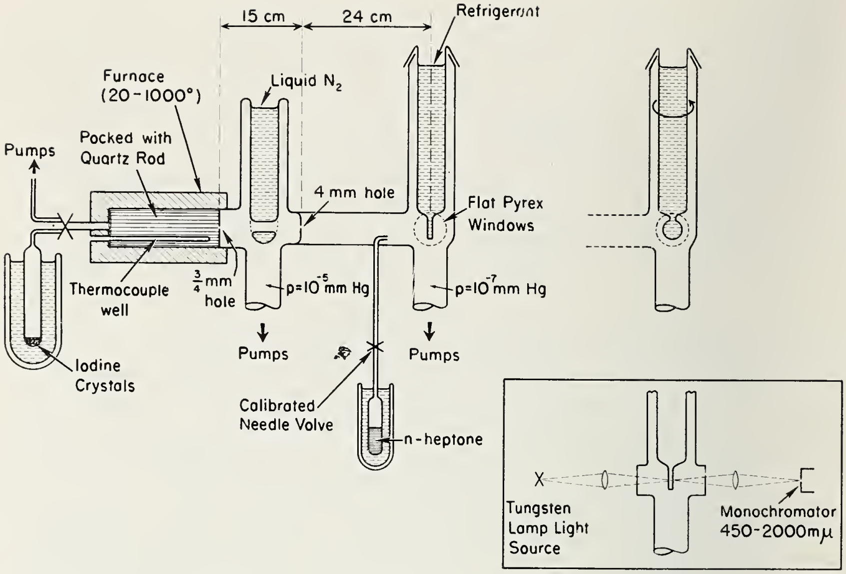


FIGURE 3. *Iodine atomic beam apparatus.*

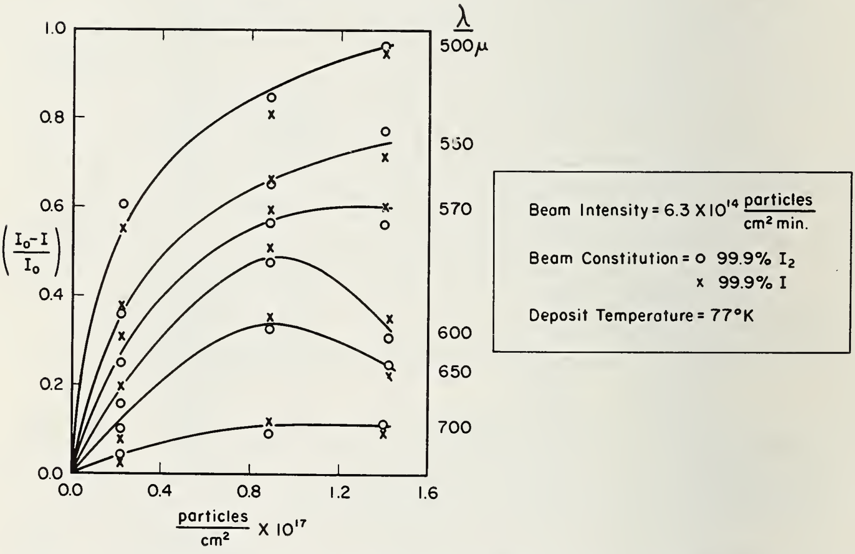
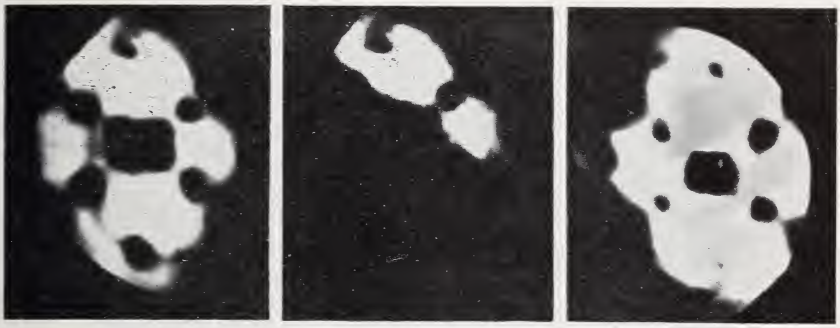


FIGURE 4. *Adsorption characteristics of condensed films of iodine atoms and molecules.*

field emission microscope. The migration of carbon monoxide [14] was investigated in a field emission tube operating at liquid helium temperature. The tungsten surface upon which the carbon monoxide was condensed, could be maintained at any desired temperature above that of liquid helium [15]. Three temperature regions for migration were observed. This is shown in figure 5. The most mobile molecules are those bound by van der Waal's forces. Thus, the mobility of carbon monoxide over carbon monoxide takes place at a conveniently observable rate at temperatures lower than 20° K. On the other hand,



CLEAN TUNGSTEN SHADOWED SPREAD

SPREADING OF VAN DER WAALS' LAYER BELOW 30° K

200° K 425° K

MIGRATION OF "WEAKLY" CHEMISORBED LAYER ABOVE 200° K

5 SECONDS 15 SECONDS 95 SECONDS

MIGRATION OF "STRONGLY" CHEMISORBED LAYER ABOVE 835° K

Figure 5. *Some characteristic surface phenomena of carbon monoxide adsorbed on tungsten observed with the field emission microscope.*

mobility in the chemisorbed layer commences only at 200° K for the more weakly bound surface state and at 650° K for the more strongly bound one. These studies serve to emphasize the complexities of diffusion controlled reactions, of which radical-radical reactions are typical.

It is feasible to extend field emission microscope techniques to the investigation of chemical reactions at low temperatures. An atomic hydrogen beam source has been set up in conjunction with a field emission microscope, figure 6. Surface reactions between an initially

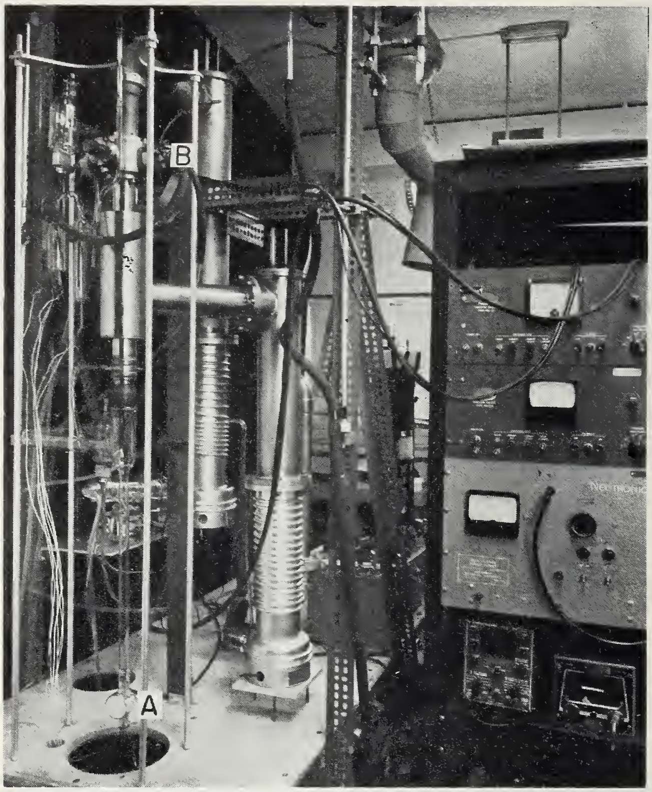


FIGURE 6. *Apparatus for the study of hydrogen atoms in the field emission microscope.*

A, The field emission microscope, attached to the atomic beam apparatus. In operation it is surrounded by liquid helium; B, The furnace for dissociating hydrogen.

deposited layer of a suitable reactant, such as oxygen and hydrogen atoms, may then be studied in the low-temperature region.

4. Photolytic Techniques

Photolysis of solids at low temperatures is sometimes useful in initiating reactions below 150° K. A. Leifer [17, 18] has deposited hydroxylamine hydrochloride and hydrazine hydrochloride on CsBr and NaCl disks by sublimation. The films so obtained were irradiated with 1849 A radiation at 77° K for 1 to 3 days. Infrared examination showed that decomposition was considerable. The major product was identified as NH_4Cl in each case. It is conjectured that the initial photolytic act is the breaking of the N—N bond in the $NH_2—NH_3Cl$ or the N—O bond in $OH—NH_3Cl$ to give radicals. $\cdot NH_3^+Cl^-$ is then presumed to abstract hydrogen to give the observed NH_4Cl.

Schnepp and Dressler photolyzed 0.3 mol percent ammonia in an argon matrix at 4.2° K below 2000 A. Both NH and NH_2 were observed by absorption spectroscopy. NH_2 disappears close to 20° K, whereas NH is still observable up to 36° K. Photolysis at 20° K is approximately five times less efficient than at 4.2° K. NH and NH_2

formation both increase at first and then level off, an indication of the independence of their formation processes.

A valuable contribution to low temperature chemistry has been made by J. R. McNesby [19] at the National Bureau of Standards, by photolysis of liquids in the region of 80° K. Oxygen, in solution in liquid nitrogen or in liquid carbon monoxide was photolyzed with predominantly 1849 A radiation. Ozone and nitrous oxide were found in the former and CO_2 and some ozone in the latter system. The products may be accounted for on the basis of the following reactions:

$$O_2 \xrightarrow[1849\ \text{A}]{h\nu} 2O(^3P) \tag{1}$$

$$M+O(^3P)+O_2 \longrightarrow O_3+M \tag{2}$$

$$O_3 \xrightarrow[2537\ \text{A}]{h\nu} O_2(^1\Sigma_g^+)+O(^1D) \tag{3}$$

$$M+N_2+O(^1D) \longrightarrow N_2O+M \tag{4}$$

$$M+CO+O(^1D) \longrightarrow CO_2+M. \tag{5}$$

As noted by McNesby, if "hot atom" effects can be shown to be absent, this method promises to be a valuable tool in the study of certain elementary reactions.

There is a low-temperature reaction between copper and oxygen from a discharge. Krugar and Ambs [16] prepared a sphere of pure single-crystal copper. Tank oxygen, discharged at 2,450 Mc and condensed on this sphere at 4.2° K, reacted with it as evidenced by pitting of the copper surface, figure 7. X-ray diffraction analysis showed that the reaction product was $Cu(NO_3)_2$. When high-purity oxygen (99.998%) was used, no pitting was observed, but a 20 A film, presumably the oxide, was found on the copper. The mechanism of the reaction has not been determined, but the application of quantitative techniques to observations of film formation promises to extend the understanding of this interesting reaction. These film thicknesses are being accurately measured with an ellipsometer so that the buildup of the copper oxide formed on the copper with condensed oxygen from a discharge can be followed.

5. Gas-Solid Interactions

A new and extremely promising technique in low-temperature chemistry resulted from the finding that hydrogen atoms, produced in the gas phase diffuse into and react with a variety of condensed solids at low temperatures [20, 21, 22, 23]. The experimental method is the exposure of solid films of substances such as olefins, oxygen, or halogens to hydrogen atoms produced by the dissociation of hydrogen on a hot tungsten ribbon. (Reference [21] gives experimental details.) The reaction can be followed by measurement of pressure decrease of the hydrogen or spectroscopic analysis of the films, in addition to the analysis of the warmed-up products. This method is valuable because a variety of low temperature reactions can now be studied quantitatively. The temperature and physical state of the reactants are

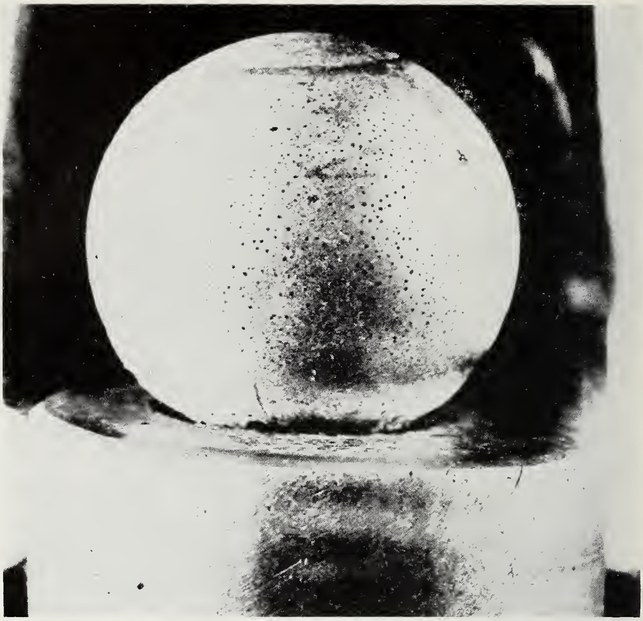


Figure 7. *Copper spherical single crystal pitted by bombardment with oxygen atoms.*

specified, the extent of the reaction in time is determinable, and variables such as the radical flux can be fixed.

Examples of some of the results may be given. Olefins differ in their reactivity at 77° K. Olefins having no terminal double bonds, such as butene-2, do not react. Propylene, butene-1, and 3 methyl butene-1 react quite readily. Hexene-1 shows no reaction. The differences are ascribable to differences in activation energy or pre-exponential factor for the primary step of H atom addition, for the diffusion of H atoms through solid hydrocarbons at liquid nitrogen temperatures occurs quite readily and is not rate controlling. The rate of reaction is directly proportional to the concentration of olefin in the solid, dilution being effected initially by admixture with the corresponding alkane (fig. 8). Inert hydrocarbon films up to 1 μ can be deposited over the reactive olefin film before a diminution in rate is observed.

From experiments with the addition of deuterium atoms to solid propylene at 77° K, the occurrence of doubly deuterated propane in the products suggested that propyl radicals might build up to a measurable concentration in the solid. There are two paths for the formation of the saturated alkane; one is the consecutive addition of two atoms, and the second is a disproportionation of two alkyl radicals to give the original olefin and the saturated alkane. By far the greater proportion of the alkane formed in the latter case should be the singly deuterated variety, however. Consecutive H atom addition implies at least a transient existence of propyl radicals. Therefore, films of solid propylene at 77° K, exposed to H atoms for varying lengths of time, were carefully examined with an electron paramagnetic resonance spectrometer [24]. No signal was ever obtained. The steady state concentration of radical species must be below the limit

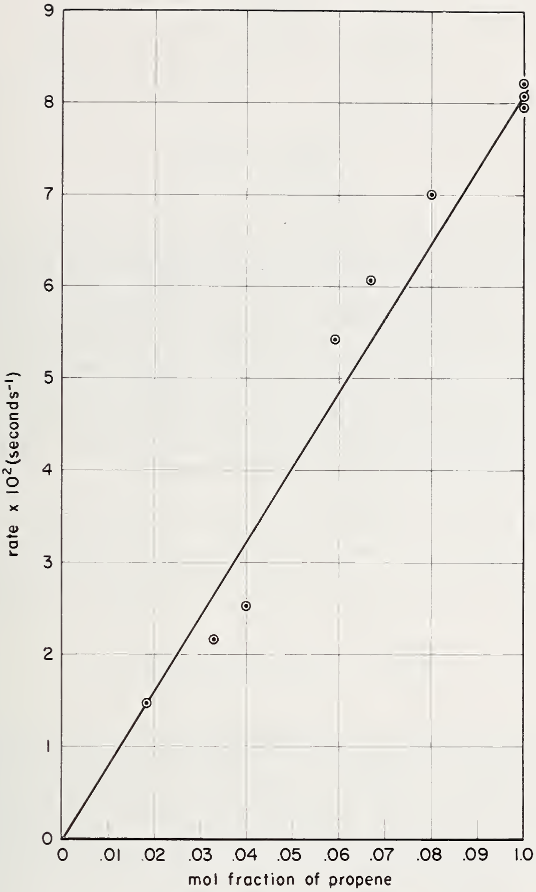


FIGURE 8. *Rate of hydrogen uptake by solid propene at 77° K as a function of concentration. Propane is the diluent.*

of detectability of the instrument, or 10^{12} spins. This corresponded to a concentration of less than one free radical in 10^7 molecules in these experiments. Two other compounds, of the aromatic type, toluene and unsymmetrical diphenyl ethylene, also gave negative results. Both added H atoms at 77° K. In spite of the possibility of increased radical stability by resonance, free radical buildup in the solid did not occur.

The general picture that emerges is that hydrogen atoms, diffusing readily through the film, react with the olefin and with the radical formed. The rate is linearly proportional to the concentration of both H atoms and olefins. The reaction is temperature dependent. It is interesting to examine the temperature distribution in the solid in order to determine the seriousness of the departure from isothermal conditions during the reaction. A hydrogen atom adds to an olefin with a heat release of about 35 kcal/mole. It is assumed that the olefin exists as an infinite isotropic continuous medium initially at 77° K. A point source of heat $Q \rho c$ calories, where ρ and c are the density and specific heat of the medium, is applied to the origin at $t=0$. The temperature as a function of the distance from the origin is

$$\Delta T=\frac{Q}{8(\pi kt)^{3/2}}\,e^{-r^2/4kt} \qquad \text{which at } t=\frac{r^2}{6k}$$

has its maximum value [25] of

$$\frac{Q}{8\left(\frac{\pi}{6}\right)^{3/2} r^3}\,e^{-3/2}.$$

The r for $\Delta T=10°$, which in the case of propylene would be the melting point if the initial temperature were 77° K, is calculated to be approximately 18 A. The relaxation time is of the order of 10^{-13} sec for these small radii, however. The assumption of isothermal conditions does not appear to be seriously in error. Application of the ordinary heat conduction equation shows that even for the production of heat of 1 cal/cm^3 sec, corresponding to the maximum rates of hydrogen pickup observed, significant temperature gradients cannot be maintained in olefin films 0.1 μ thick.

A descriptive model follows for the reaction of atoms introduced at the surface of a low-temperature solid which can react with the free radical atomic species, expressed in terms of the reaction of hydrogen atoms with olefins. The observable is the rate of pressure decrease in the gas phase. If a layer of solid of thickness l, is considered,

$$\frac{-dH_2}{dt}=\frac{A}{2}\int_0^1 [k_1(\text{Ol})(\text{H})]dx.$$

This expresses the rate of hydrogen uptake in terms of the reaction between H atoms and the olefin (Ol) arising from H atom addition to the olefin. A is the area of the film. The factor ½ arises from stoichiometry. Hydrogen atoms diffuse readily through these films so that the concentration at any level X may be described by the diffusion equation including the appropriate chemical reaction term:

$$D\,\frac{\partial^2 \text{H}}{\partial x^2}=\frac{\partial \text{H}}{\partial t}+K\text{H} \qquad \text{where } K=k_1(\text{Ol}).$$

It is assumed that the reaction does not occur to such an extent that there is an appreciable change in the olefin concentration. The H atom recombination term, $K'\text{H}^2$ is not included, for the inert layer experiment shows that in the film thicknesses and H atom concentrations used in these experiments, the recombination reaction is negligible. Under the boundary conditions

$$\text{H}=\text{H}_0 \text{ at } x=0$$

$$\frac{\partial \text{H}}{\partial x}=0 \text{ at } x=l$$

$$\text{H}=0 \text{ at } t=0$$

there is obtained

$$\frac{dH_2}{dt}=-\sqrt{DK}\,\text{H}_0 \tan h\,\sqrt{\frac{K}{D}}\,l$$

neglecting the transient term. For relatively thick films, this is essentially constant and equal to

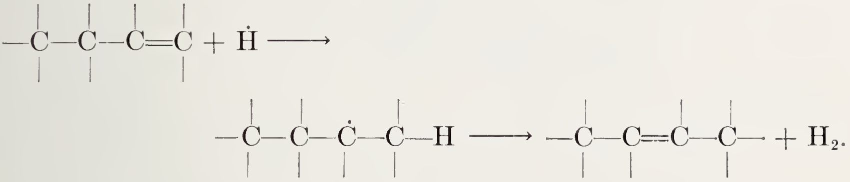
$$-\sqrt{DK}\,H_0.$$

On the other hand, for thin films

$$\frac{dH_2}{dt}=-KH_0l,$$

so that the rate should be proportional to film thickness. Appropriate rate measurements can be interpreted in terms of a rate constant for the elementary addition reaction and a diffusion coefficient for volume diffusion of hydrogen atoms in the solid.

Besides addition of an H atom to a double bond, another low-temperature reaction was found to be hydrogen abstraction from an alkyl radical by hydrogen atoms [26]. Since abstraction of a secondary hydrogen is favored, the result of the process is a double bond isomerization in which there is a double bond shift from a internal position. Butene-1 is isomerized to transbutene-2 at 77° K, for example,



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\overset{|}{C}=\underset{|}{\overset{|}{C}}+\dot{H}\longrightarrow -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\dot{C}}-\underset{|}{\overset{|}{C}}-H\longrightarrow -\underset{|}{\overset{|}{C}}-\underset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-+H_2.$$

Butene-2 does not react at 77° and hence accumulates in a film of solid butene-1 exposed to H atoms. If a film of butene-1 is reacted with D atoms under the same experimental conditions, HD can be observed to increase in the gas phase so that the given reaction is established. It is interesting to note that although butene-1 and 3, methyl, butene-1 give HD with D atoms, propylene or alkanes including those with tertiary hydrogens do not. The absence of HD formation in the case of propylene implies first, that abstraction of a primary hydrogen does not occur, and second, that abstraction of a secondary hydrogen attached to a carbon with an unpaired electron does not take place. The energy requirement is probably too high for the first.

A low-temperature H atom addition reaction, observed at 20° K, is that between H atoms and solid oxygen [27]. The reaction is effected in an apparatus as shown in figure 9, using liquid hydrogen as the refrigerant. Reaction was followed by observing the pressure decrease of the hydrogen in the vessel, and also by mass spectrometric analysis of the warmed-up products. Traces of hydrogen peroxide were detected by a yellow color with $TiCl_4$ solution. The reaction undoubtedly occurs by way of an initial addition of a hydrogen atom to an oxygen molecule to give the radical HO_2, but because HO_2 can react further with H atoms,

$$HO_2+H \text{———} 2OH$$

$$OH+H \text{———} H_2O$$

it is not likely that HO_2 can be stabilized under these conditions.

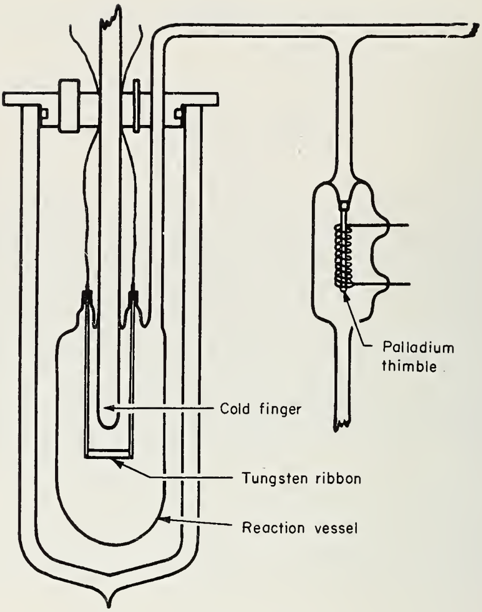


FIGURE 9. *Apparatus for the investigation of the hydrogen atom-solid oxygen reaction at 20° K.*

6. Special Techniques

An apparatus, figure 10, has been built by Thomas [28] to study reactions resulting from solids bombarded with free radicals. This consists of a highly polished, rapidly rotating stainless steel cylinder containing liquid helium. At one point gases such as oxygen or olefins are deposited in molecular beam fashion. Diametrically opposite, the film is bombarded, again in molecular flow, with free radicals.

A method of inducing chemical reactions in systems below 150° K is electron bombardment of the condensed solid [29]. The apparatus is shown in figure 11. Mixtures of $N^{14}N^{14}$—$N^{15}N^{15}$ were exposed to an electron beam of 15 kv at current levels of 5 to 10μ amp. The extent of reaction was determined with a mass spectrometer by the $N^{14}N^{15}$ formed. The radiochemical *G* value based on the exchange process at 4.2° K is about 0.2. At 20° K this drops to 0.04. The formation of $N^{14}N^{15}$ results from atom recombination as well as possible excited molecule or ion reactions.

Gamma irradiation of solids at low temperature with a cobalt-60 source has been used in preparing stabilized free radical systems [30]. Nitrogen, hydrogen, deuterium, and methane have been irradiated, and in each case free radicals were found to be present using the electron paramagnetic resonance spectrometer. It was observed that in the case of hydrogen, a decrease in the hydrogen atom concentration occurred on storage. This would indicate that H atoms are somewhat mobile in a molecular hydrogen matrix even at 4.2° K. Gamma irradiated methane at 4.2° K was interesting in

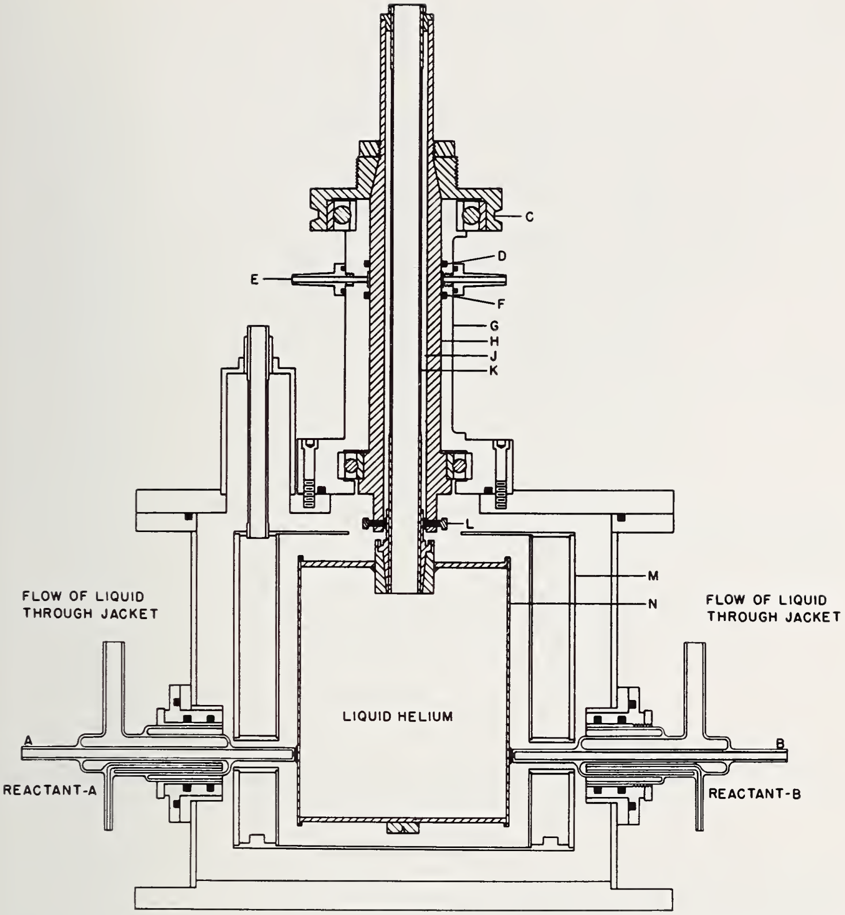


FIGURE 10. *Rotating Dewar for the study of radical molecule reactions at low temperatures.*

that an electron paramagnetic resonance spectrum of both CH_3 and H were obtained. Momentary warming of the sample to 20° K and recooling to 4.2° K resulted in the disappearance of H but no diminution in CH_3. This result is difficult to interpret unless either a nonzero activation energy or a large steric factor applies to the $H+CH_3$ recombination at 20° K.

Only brief mention is made here of the extensive studies of photolysis in rigid solvents at low temperatures. An excellent review paper by Linschitz [31] summarizes work done in photo-dissociation, excited states, photo-reduction and photo-ionization processes.

Many catalytic processes can occur in the low-temperature region. The classic experiment of Bonhoeffer and Harteck [32] on the conversion of ortho- to para-hydrogen on charcoal at liquid air temperature is one of the earliest examples. Gould, Bleakney, and Taylor [33] showed that Cr_2O_3 and Ni catalyze the hydrogen-deuterium exchange even at −190° C, while Eley [34] found that a tungsten

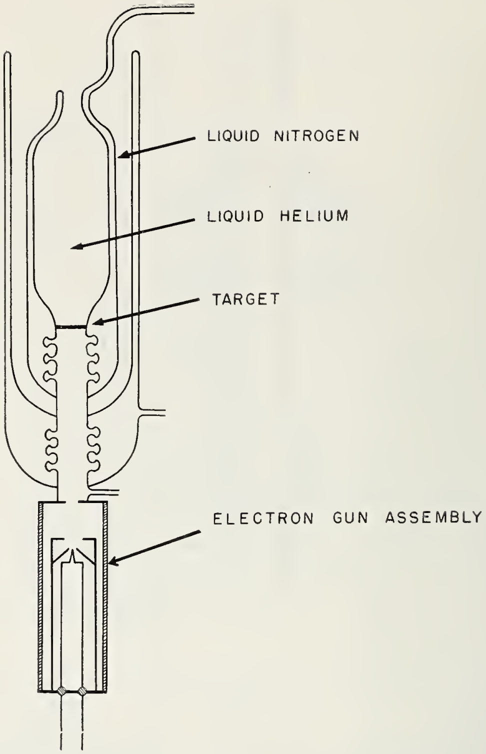


Figure 11. *Apparatus for investigating reactions at liquid helium temperatures induced by electron bombardment of condensed solids.*

surface was effective for both the ortho-para conversion and the hydrogen-deuterium exchange at 77° K.

Although low-temperature chemistry is in an early state of development, recent activity indicates that considerable further progress may be expected. This includes the elucidation of elementary reactions and an experimental approach to concomitant problems of diffusion, energy exchange, and free radical stabilization.

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WASHINGTON 25, D.C., December 9, 1959.

6. Methods of Production of Trapped Radicals and Properties of Radical-Trapping Solids

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1. Introduction

Numerous reviews describing methods of producing trapped radicals have appeared within the last few years. In particular, two excellent reviews have been written very recently: The first by B. A. Thrush [1][2] deals with radicals formed in the gas phase before being trapped; and the second by G. C. Pimentel [2] deals with production of trapped radicals within solids. These reviews describe the subjects very comprehensively and so recently that there is little point in covering exactly the same ground here. Instead, since the burden of complete description and historical introduction has been shouldered by these previous authors, the opportunity is taken of concentrating upon the principles underlying the trapping of radicals rather than on details of the work of individuals. Emphasis is placed on the mechanism of trapping, and work in the field is described only insofar as it throws light on the processes involved.

2. Trapping of Radicals—the Trapped State

In the first place what is meant by a "trapped radical"? All that is meant in this paper is a radical which is stored in such manner that it cannot recombine with another radical even though in other circumstances it would recombine with liberation of much energy.

Trapping, then, is the storage of radicals such that they do not recombine over an indefinitely long time.

2.1. Recombination of Radicals

Radicals recombine with each other at a rate which, like that of all bimolecular chemical reactions, is the product of three quantities: (1) The number of collisions between radicals per second; (2) the fraction of such collisions which possess some minimum amount of energy; and (3) the probability that fruitful reaction will result from a collision of sufficient energy.

For complete inhibition of recombination, i.e., for successful trapping, at least one of these terms must be reduced to zero.

a. Prevention of Collisions Between Radicals

Collisions between radicals in solids can be prevented by isolating radicals within a matrix of inert material such that diffusion of the radicals within this matrix is reduced to a negligible amount. This point has been amply made by Whittle, Dows, and Pimentel [3], Norman and Porter [4], and other authors.

It is not enough merely to contain the radicals within solids, for diffusion within solids, particularly of small radicals, can take place quite rapidly. Klein and Scheer [5] have shown that diffusion of

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[2] Figures in brackets indicate the literature references at the end of this paper.

hydrogen atoms in thin films of solid olefins at 77° K is not even a rate-controlling process in the hydrogenation of the olefins. (However, when films of inert hydrocarbons of 10^{-4} mm thickness, and greater, are placed between the reactive olefin and the source of atoms, then some inhibition of reaction rate takes place. The experimental method thus holds promise for providing badly needed information on diffusion coefficients of radicals in solids.)

Many authors have described experiments where radicals have recombined at temperatures well below the softening point of the matrices in which they were embedded. For example by making electron spin resonance (ESR) measurements Livingston, Zeldes, Weinberger, and Holmberg [6] detected hydrogen atoms in γ-irradiated samples of solidified mineral acids at low temperature. The ESR signal attributed to these atoms disappeared when the solids were warmed to temperatures which were still well below their softening points.

There is some evidence to show that diffusion of radicals is completely prevented when they are trapped, but such evidence is restricted to large complex radicals. Lewis and Bigeleisen [7] photolyzed various substituted benzidenes with plane polarized ultraviolet light and showed that the colored radicals formed absorbed polarized light most strongly when the plane of polarization was parallel to that of the exciting light. The radicals were thus shown to be held very rigidly in their environment. Furthermore Ghosh and Whiffen [8] have shown that radicals formed by irradiation of a single crystal of glycine are precisely alined (and therefore rigidly held) within the crystal. It may be worth pointing out, however, that such experiments do not conclusively show that prevention of diffusion is an *essential* prerequisite for trapping. For such a demonstration we need a convincing correlation between rates of diffusion and lifetimes of radicals in a matrix.

b. Energy of Activation of Recombination of Radicals

The literature abounds with statements that no energy of activation is needed for recombination of radicals. Thus Hinshelwood [9] states "For a reaction between two atoms such as Cl or Br no activation can be required." Or Semenov: [10] "Processes of recombination of free radicals proceed in the majority of cases with no activation energy." Or Steacie: [11] ". . . in general there is no activation energy for reactions in which two atoms or free radicals combine." But these statements should be taken in their context which is discussions of gas phase reactions at and above room temperature where activation energies of say 0.25 kcal/mole would be wholly negligible. On the other hand at 4.2° K and below, 0.25 kcal/mole would present a formidable energy barrier to reaction and it is essential to give careful consideration to whether in fact there may not be some small activation energy for radical-radical reactions. Even if no activation energy is needed for gas phase recombination, would the same hold true for radicals diffusing in a solid? There is very little experimental evidence on the subject, which is not surprising for the experimental techniques for such an investigation would be extremely difficult. The question is unanswered but is vital to the whole field of low-temperature chemistry.

c. Probability of Recombination When Collision with Requisite Energy of Activation Takes Place

Radical-radical reactions in the gas phase are affected by two factors. One of these is the necessity for a third body in the recombination of atoms and very simple radicals to prevent the molecule formed on collision from immediately redissociating [12]. Complex radicals do not need this third body for they possess many internal degrees of freedom which can accommodate the excess energy sufficiently long for it to be removed in a single subsequent collision. (Reference will be made again to this third body effect when discussing the trapping of radicals from gases.) The other factor is a true steric effect which appears to be small for simple radicals, but which may become large for complex species.

Both these factors are drastically altered in solids. There are always third bodies present so that recombination of simple radicals are no longer hindered through lack of an energy receptor, but on the other hand, true steric effects may become very much more important. For example one may consider the recombination of methyl radicals. The steric factor for recombination in the gas phase has been estimated from experimental results to be about 10^{-1} or higher [13]. One can reasonably imagine that the radicals, which have a planar or nearly planar configuration, may need to face each other in order to react. This they may do in the gas phase where molecular rotations are unhindered with a probability of 1 in 10 or higher. (This assumes that the factor is purely and literally a "steric" one.) If now the radicals are diffusing in a solid lattice it seems reasonable to picture them as much more likely to move edgeways through the lattice, than in a line perpendicular to their plane shape. This will be so if molecular rotation about an axis through the plane of the molecule is hindered. Thus collisions between two methyl radicals in solids may take place exclusively at the edges of the planes; and reaction may become far less probable than it was in the gas phase. There is some evidence in the work of Wall, Brown, and Florin [14] that even hydrogen atoms may not react very efficiently with methyl radicals in solid methane.

An attempt at reducing the probability of reaction between radicals by alining the spins of the unpaired electrons so that they are all parallel to one another has been made independently by Fite [15] and Windsor [16]. They produced molecular beams of partially dissociated hydrogen and by means of very strong inhomogeneous magnetic fields split these beams into three separate beams: one of undissociated molecules; one of atoms with electron spins alined in one direction; and one of atoms with electron spins alined in the other direction. If these beams are condensed separately, and if the alinement of spins can be preserved during the condensation process and in the resulting solid, high concentrations of trapped atoms might be achieved. However, results so far reported by Fite, indicate that few atoms survive the condensation process without recombining.

3. Generation of Free Radicals

The chemical processes in which free radicals are formed are very similar in both solids and gases. It is thus convenient first to describe these processes generally and then to examine features peculiar to the different phases.

The only way in which radicals (excluding triplet states of molecules) can be initially produced from stable molecules is by dissociation. Subsequently these radicals may decompose, or may add on to saturated molecules, or may abstract part of a saturated molecule leaving the remainder as a free radical. The primary act however is dissociation, which results from the acquisition by a molecule of sufficient energy to break one of the bonds holding the molecule together. This energy can be obtained either by collision, or by interaction with radiation.

3.1. Dissociation Resulting from Collision

a. Collision with Molecules—Thermal Decomposition

Much of the early work on free radicals, especially the extensive investigations of F. O. Rice and his coworkers, [17] was directed at understanding the thermal decomposition of organic compounds. Methyl, and to a lesser extent ethyl, radicals were shown to be products of thermal decomposition. More recently Scheer [18] has worked with atomic iodine produced from molecular iodine in a furnace, and Robinson [19] has used nitrogen dioxide prepared essentially by pyrolyzing dinitrogen tetroxide. Hydrogen atoms are also conveniently prepared by thermal decomposition on a tungsten filament, a well-known method that has recently been used by Klein and Scheer. [5] Klein [20] has also constructed a high-temperature furnace from which hydrogen atoms emerge in known concentration in a molecular beam. The method can be employed reasonably where appreciable dissociation takes place at easily attainable temperatures. It has been naturally used mainly, if not exclusively, with gases for the simple reason that at the temperatures necessary for dissociation the species are gaseous.

b. Collisions with Electrons and Ions—Electrical Methods

Whereas dissociation by the use of thermal energy is a process that has been restricted to gases, dissociation by the use of electrical energy has been applied to solids as well.

In the gas, electrical discharges are generally used. Microwave discharges, other high frequency electrodeless discharges, and discharges between electrodes all produce somewhat similar results, though some methods work better in some ranges of pressure or in some gases than others. It has been shown [21] that discharges between electrodes can result in contamination by the electrode material, but in many applications this may not be a serious drawback. Electrical discharges are very convenient experimentally but they result in a wide variety of labile products, namely ions and radicals in various excited states and also excited molecules. The exact process by which radicals are produced is not at all clear, but it must involve collisions with charged species moving at high velocities which have been achieved by acceleration in a steep potential gradient. Furthermore it is not possible to estimate (as it is for thermal dissociation) the concentration of radicals produced.

Processes of controlled electron bombardment of gases do not seem to have been much used in work on trapping of radicals, though they are used very extensively in mass spectrometers, and there is precise information on the nature of the charged molecular fragments produced.

Discharges have also been applied to solids and again seem to be somewhat indiscriminate with the further complication that the actual locality where the discharge strikes is by no means clearly defined.

Rebbert and Schoen [22] have applied high d-c potentials from a sharp pointed electrode in a high vacuum to solidified mixtures of oxygen in various matrices. Considerable light was emitted during the ensuing passage of current, and the emission was characterized as similar in many respects to that emitted during condensation of gases which had passed through discharges (Peyron and Broida [23]). This emission has been attributed partly to excited molecules and partly to excited atoms. Vegard [24] used well-defined beams of ions or electrons in his classical work on the emission produced by the impingement of these beams on solid nitrogen and rare gases. McLennan and Shrum [25], and more recently Alger and Anderson [26], and also Hörl [27] have controlled and refined the bombardment by electrons of solid species. Electron bombardment of solids appears to be capable of greater control than other discharges since both the energy of the electrons and the area of bombardment can be well defined.

3.2. Interaction with Radiation

Ultraviolet light, X-rays, and γ-rays have all been used to dissociate molecules in the solid phase, but only ultraviolet light has found much application with gaseous molecules.

Photolysis is a very discriminating process: by the use of suitable wavelengths of irradiating light and suitable absorbing substances, the nature of the dissociating process and the identity of the subsequent fragments may be fairly well known. In fact Porter, Chilton, and Strachan [28] have photolyzed in rigid solvents groups of various compounds, chosen deliberately, and found by absorption spectroscopy that the same radical was produced from all members of the same group.

Radiolysis, i.e., the absorption of X-rays and γ-rays, would be expected to break bonds indiscriminately because the quanta of energy absorbed are very large. In practice however, radiolysis may be remarkably specific in its effect. Porter, Chilton, and Strachan [28] report that irradiation of triphenyl methane in solid aliphatic solvents results in dissociation of the solute in an amount greater than could be explained without postulating transfer to the solute of energy initially absorbed by the solvent. Thus though the radiation may have been absorbed indiscriminately, the products finally formed were far more specific.

X-rays, used by Alger and Anderson [26], and γ-rays used by various workers [29, 6, 13] have been very successfully used for the production of well defined radicals at very low temperatures. In all these cases, the detection of radicals was by ESR spectroscopy which is sensitive only to compounds with unpaired electrons. Thus, provided the number of radical species was small, it did not matter how complex was the mixture of stable products of irradiation.

Vacuum ultraviolet photolysis is a promising new method for radical production. It is more universally applicable than photolysis at longer wavelengths for there are many more substances which absorb in the vacuum ultraviolet than do in the visible and near ultraviolet. Nelson and Ramsay [21] have recently produced a variety of free radicals by such photolysis of gases, and Dressler and Schnepp [30] have succeeded in trapping NH and NH_2 by photolyzing ammonia in solid argon.

3.3. Secondary Radical Formation

So far, we have discussed dissociation, which is the primary process for forming radicals. Other radicals may be formed in secondary reactions. A radical may decompose to form a small radical and a stable molecule; or in reverse a radical may add on to a stable molecule to form a larger radical; or again, a radical may abstract a portion of another molecule to satisfy its own free valence, and leave the remaining fragment of the molecule as a new free radical. These types of reactions in the gas phase have received considerable discussion Steacie [12], Thrush [1], and we shall return to them in a later section.

4. Trapping Radicals from Gases

Most free radicals have extremely short life times in the gaseous phase: recombination takes place so rapidly that appreciable concentrations of radicals can have but a very transient existence. Exceptions to this generalization are: (a) Radicals which can exist in thermal equilibrium with their dimers, e.g. NO_2, I, and certain resonance-stabilized aromatic radicals; (b) very simple radicals which require three body collisions for recombination, such as H, N, and O; and (c) radicals in a molecular beam where they are largely isolated from collision.

It is only with these exceptions that there is well-founded hope of trapping appreciable quantities of radicals out of the gaseous phase.

Further difficulties arise during condensation, for this process has requirements which are somewhat incompatible. On the one hand all the translational energy of the radical must be lost, which can only be through collisions, and on the other, recombination during collisions must be prevented.

Furthermore there may not be a direct transition from gaseous phase to solid phase. Even though the liquid phase may not intervene, there is likely to be considerable migration of molecules and radicals over the surface of the solid with great frequency of collision with other migrating and fixed molecules, all being effectively "three-body" collisions. Thus even if the radicals arrive unscathed into a condensed phase, they stand a good chance of recombining before they are finally trapped.

The optimum conditions for trapping would seem to be as follows: (1) Radicals must lose their translational energy in as few collisions as possible and should stick without migrating around the surface; and (2) radicals should not alight on other radicals, but on inert molecules, and should then be protected from following radicals by a surrounding sheath of inert molecules.

The best illustration of the principles discussed here is provided in the work of Robinson and McCarty [3] who succeeded in trapping diatomic and even triatomic radicals from the gas phase. The initially stable molecules were mixed with a large excess of inert gas and then passed through a discharge. The products emerged into an uncollimated molecular beam and then impinged on a very cold surface. The rate of deposition was kept very small so that thermal gradients through the deposit would be small, and the outer surface would remain cold. Thus migration on the surface would be kept to a minimum. By such means were prepared an impressive array of radicals which were identified by ultraviolet and visible absorption spectroscopy.

Unless the radicals are monatomic and require third bodies for recombination it seems essential to provide great dilution or molecular beam conditions, or both, to enable them to survive transport to the cold surface, and subsequent condensation. There may be very little chance even so of trapping polyatomic radicals greater than, say, ethyl by such a scheme. Attempts to trap large reactive radicals produced during thermal decomposition of organic materials have so far been unsuccessful.

Comeford and Gould [32] passed azoethane in argon at low pressure through a furnace, and rapidly condensed the products of pyrolysis on a cesium iodide window cooled by liquid helium. Infrared absorption spectra indicated the presence of ethylene and ethane in the solid film but no azoethane, no *n*-butane, and no bands attributable to alkyl radicals. The gases obtained on evaporating the condensate nevertheless contained an appreciable quantity of *n*-butane which would certainly have been detected in the solid film if it had existed there. This evidence has been taken to indicate the presence in the film of labile species, the exact nature of which remains to be discovered.

5. Trapping Radicals that are Generated in Solids

5.1. Cage Effect

When radicals are produced within the structure of solid material the complexities that relate to trapping from gases disappear, and are replaced by a somewhat simpler problem. This problem is simply that dissociation leads to *two* free radicals, and not just one. Whereas in the gas phase the two radicals fly apart freely, in the solid phase they are more constrained to remain together, and stand a chance of recombining immediately. This is known as the cage effect, and was proposed by Franck and Rabinowitch [33] to explain some very low quantum yields during photolysis. Whether this cage effect is significant in a particular process will depend on the ease with which the radicals can move apart after they are formed. This in turn would seem to depend on: (a) The surplus kinetic energy possessed by the two fragments after separation; and (b) the diffusion coefficients of the fragments. Thus if one fragment is a hydrogen atom it may be very easily lost. Lewis and Lipkin [34] were nevertheless able to prepare diphenyl nitrogen radicals, which are large and unlikely to diffuse rapidly, by photolysis of tetraphenyl hydrazine in a rigid solvent. Linschitz [35] has pointed out that in this case simple changes in relative orientation of the fragments could result in stabilization. Porter and his coworkers [36] report little evidence of a cage effect in their work. Pimentel [2] however in a lengthy discussion of the subject points out evidence demonstrating a substantial cage effect and suggests that little decomposition occurs during photolysis unless the fragment trapped is very stable, or the other fragment reacts with the matrix.

Even if the matrix allows effective dissociation, it is still necessary that it should trap one of the radicals formed. Leifer [37] has photolyzed crystalline hydrazine hydrochloride and hydroxylamine hydrochloride at 77° K up to the point of complete decomposition, and at 20° K to a lesser extent, yet infrared absorption spectroscopy has shown no sign of intermediate products or labile species, and ESR measurements have indicated only a trace of free radical content.

5.2. Secondary Reactions

If the solid matrix is itself reactive, then secondary radicals may be formed by reaction between primary radicals and the matrix material. Gibson, Ingram, Symons, and Townsend [38] have exploited this possibility by freezing dilute solutions of hydrogen peroxide in various solvents and photolyzing the solids. Hydroxyl radicals are first formed which then react with the solvent (mainly alcohols) abstracting hydrogen to form water, and leaving a solvent radical. The technique seems very versatile, and greatly extends the range of radicals that can be produced by photolysis.

Klein and Scheer [5] have reacted frozen olefins with atomic hydrogen. Analysis of the products demonstrated conclusively that alkyl radicals had been produced, even though none was stabilized. In the circumstances of their experiments where hydrogen atoms were bombarding a thin film of olefin it was likely that hydrogenation would go to completion: a hydrogen atom would react with an alkyl radical in preference to an unattacked olefin because of the lower activation energy that would be needed. Thus the alkyl radicals would not survive.

Thomas [39] is attempting to overcome this difficulty in the reaction of gaseous radicals with solid surfaces by laying down a very thin layer (less than a monolayer) of atomic hydrogen upon a thicker layer of a solid reactant. The atomic hydrogen layer is then covered with another thick layer of the reactant, and the process repeated, building up a "multideck sandwich." This is achieved by depositing the two reactants on diametrically opposite sides of a swiftly rotating cold cylinder.

6. Desirable Properties of Radical-Trapping Solids

Some of the desirable properties of the medium in which free radicals are trapped are common to both trapping radicals from gases and trapping radicals in situ. They are suggested by considerations of the nature of the trapped state, and of the purpose of the experiments. Other desirable properties are peculiar to the method of trapping.

6.1. Low Temperature

The most important physical property is that the solid should be at low temperature. Although examples exist of radicals trapped at normal temperatures (e.g., by the occlusion of radicals in polymers—and even here the lower the temperature the better the trapping) most work on species which have a great tendence to recombine has been carried out at or below the temperature of liquid nitrogen. Diffusion is slower, and activation energies are harder to come by. This is perhaps obvious, but none-the-less worth stating.

6.2. Structure of Matrix and Rates of Diffusion

The principal function of the matrix is to keep radicals apart, and this means essentially to restrict the diffusion of radicals. There is unfortunately very little information available on rates of diffusion in molecular crystals. Pimentel [2] has surveyed the temperatures at which diffusion has become observable in rigid systems (as detected by the onset of chemical reactions between previously trapped reactants) and has proposed that diffusion becomes appreciable when the temperature exceeds about one half the temperature at the melting point. He bases his figures partly on surveying some very varied experiments and partly on analogy with the work of Nachtrieb [40] on self diffusion in metals. Thus a high melting point appears to be desirable.

Such a simple relationship of diffusion coefficients to the melting point of matrices might be expected in the case of very large complex radicals. If these radicals are large compared with the lattice dimensions of the matrix crystal, then their movement will depend mainly on the viscosity of the medium, and thus will be related to the melting point. For very small radicals however, we have to consider more carefully the manner in which they are held in the solid. (Pimentel excludes small radicals from his main discussion and suggests their diffusion might take place at temperatures nearer one tenth of the matrix melting point.)

6.3. Trapping Sites

It may be helpful here to summarize some of the suggestions that have been made concerning the nature of trapping sites. It appears possible usefully to distinguish between the following types of sites, even though some of them may overlap: (a) Lattice sites, where the radical replaces one of the molecules in the crystal lattice of the matrix; (b) interstitial sites; (c) at dislocations; and (d) in holes which are left in amorphous materials like glasses. The forces involved in trapping so far are of the van der Waals type, but we may add another category of: (e) as portions of loosely bound chemical species.

A knowledge of the crystal structure of matrices is of very great value in attempting to decide what sort of sites are occupied by radicals. Bolz, Mauer, and Peiser [41] have investigated the crystal structure of condensed gases at very low temperatures by an X-ray diffraction technique. They examined gases condensed both before and after passing through discharges and also studied how the structure of the solids changed on warming. Their conclusions very briefly were that most gases condensed at low rates showed some long range order. On warming, annealing and further crystallization took place with evolution of heat. The degree of disorder was less when the gases had passed through a discharge, an effect attributed to local heating and annealing following recombination of radicals on the surface. Solids in which hydrogen bonding takes place were most lacking in long range order, and would thus contain most faults. This work provides a sound background to understanding the structure of condensed gases and is now being complemented by electron diffraction studies by Hörl [42].

A further example of the importance of the structure of a matrix is the fact that diffusion rates along one of the main axes of a crystal may be 10^6 times greater than those along another axis of the same crystal (Jost [43]).

Livingston [6] and his colleagues have shown that 20-fold higher concentrations of H atoms can be stabilized in glass-like solids than in highly crystalline ones of the same chemical composition. High concentrations of radicals might result here either from increased accommodation or from reduced mobility i.e., the total number of sites available for trapping may be greater than in a crystalline solid, or the rates of diffusion of the trapped species may be less. Another way of putting it is that both the number of sites and the magnitude of the trapping bond can influence the concentration of species trapped.

Measurements of diffusion coefficients in molecular crystals are not easy and there is a great dearth of information on the subject. A different type of measurement concerned with the rigidity of molecules in a solid is the ease with which dipoles can follow a changing electrical field. N. Brown [44] has developed equipment to make measurements of the dipole moments, and variation in power loss with frequency of an alternating electric field across solids at low temperatures. Results for solid ammonia over a range of temperatures show that the dipoles cannot follow a frequency as low as 40 cps which is the present low frequency limit of the equipment. Extension of the work to much lower frequencies would be of great interest.

6.4. Formation of Loose Compounds

If a free radical can be induced to form a loose bond with a stable molecule, then that bond might present a formidable barrier to diffusion and recombination of the radical. A bond of only 1 kcal energy would more than suffice. Perhaps the most discussed examples of such loose compounds are the H_3 and N_3 molecules which have been theoretically postulated. Experimental evidence [48] has recently been obtained to support the postulate of an N_3 (or preferably $N_2—N$) molecule.

6.5. Thermal Conductivity

The liberation of energy during condensation of gases and recombination of radicals on surfaces needs to be quickly dissipated by the matrix, which therefore should have for preference a high thermal conductivity. Little information has been published concerning the thermal conductivity of solidified gases at low temperature, but recently Roder [45] and Chatenever [46] have been making measurements independently, and with different types of equipment.

Comparison of results indicates that the structure of the solid (not unnaturally) greatly influences the conductivity, a dense deposit being the most conductive.

6.6. Properties Related to Purpose of Experiments

Selection of a matrix is very much conditioned by the purpose of an experiment. Thus if measurements are to be made of properties of the radicals, then the matrix should interfere as little as possible. For example, if absorption spectroscopy is to be used to examine the radicals then the matrix should neither absorb nor scatter (which is less easy to achieve) the radiation used (Becker and Pimentel [49]). Further, Robinson and McCarty [31] have required for their purposes that the matrix should not perturb the electron states of the trapped radical. They state it is also preferable if the matrix falls into a well ordered lattice or reproducible arrangement surrounding the radicals since random perturbations would broaden the lines of the absorption spectra which they wish to observe.

6.7. Properties Related to Trapping Radicals from Gases

Robinson and McCarty [31] have stated that the matrix must be stable in the conditions in which the radicals are produced, and must be inert to the radicals in the gaseous phase as well as in the solid.

Becker and Pimentel [49] have also stipulated that the medium should have a suitable volatility for ease of handling, while Thrush [1] has recommended good thermal conductivity of the solid for rapid cooling of the gas on the surface of already-formed deposit.

Condensing molecules need to lose their energy in as few collisions as possible, and it is consequently of great interest to examine what determines how much energy is lost in a collision between a gaseous molecule and a surface. Zwanzig [47] has given some attention to this problem and concludes that for most efficient transfer of energy: (1) The mass of the gaseous molecule should not be much less than that of the molecules of the solid; and (2) the velocity of the alighting particle should not exceed the velocity of sound in the solid.

It immediately follows that for optimum energy transfer the matrix should generally be of low molecular weight, and should propagate sound waves with great velocity.

6.8. Properties Related to Trapping of Radicals Generated in Situ

The properties needed for trapping in situ are: (1) The solid must be unaffected by the process producing radicals, e.g., it must be transparent to the photolyzing radiation; (2) it should not scatter the incident radiation; and (3) there should be little "cage effect".

As discussed earlier, Pimentel [2] suggested that the matrix could with advantage react chemically with *one* of the products of primary dissociation.

In conclusion, table 1 is presented in which many of the desirable properties of a matrix are brought together. The lack of precision in defining the most important qualities illustrates the great deficiencies in our knowledge, and underlines the directions in which future work might profitably be undertaken.

Table 1. *Summary of desirable properties of solid matrices for trapping radicals*

1. The matrix should be at low temperature.
2. It should be inert to the method of generation of radical.
3. It should be chemically inert to the radicals trapped.
4. It should not interfere with the method of analysis for the radicals, nor with measurements to be made of properties of the radicals.
5. Its structure should accommodate high concentrations of radicals—(a "glassy" structure seems to be favorable).
6. It should greatly impede diffusion of radicals by:
    (a) providing closed-in sites (again a glassy structure may be favorable) or
    (b) forming a strong localized attachment to the radical.
7. It should have a high thermal conductivity (here a compact dense structure would be favorable).
8. It should have a high melting point.
9. For trapping from gases the matrix material should:
    (a) be of low molecular weight, and
    (b) transmit sound with great velocity.
10. For trapping radicals from solids, it should allow the dissociating molecule to part, but should prevent recombination.

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WASHINGTON 25, D.C., January 15, 1960.

7. Identity and Concentrations of Trapped Radicals

Robert W. Zwanzig

1. Introduction

Many methods of identifying trapped reactive species and measuring their concentrations have been proposed. Some of these are standard ones, for example optical spectroscopy and electron spin resonance, and have been studied extensively at NBS and elsewhere. Other more unconventional methods have been investigated in exploratory work mainly at NBS. These methods all have good and bad features; some have turned out to be of little value, but a few have given useful information. In this survey a number of these methods will be discussed. Major emphasis will be put on the utility of the method, rather than on the results which have been obtained so far. Since research which has been done in other laboratories is described extensively in the scientific literature, this review shall be confined, for illustrations, mainly to work done at NBS. Since other surveys in this volume contain extensive bibliographies, no specific literature references will be given here.

Before the various methods are discussed, a brief outline of experimental results obtained during the NBS Free Radical Research Program will be presented.

The trapped radicals which have been identified with reasonable certainty at NBS are N (or perhaps N_3), H, O, NH, NH_2, CH_3, HNO. Other radicals for which there is some partial evidence, but not enough for positive identification are NH_3^+, C_2H_5, CN, HO_2, Cl. Aside from species which we are accustomed to call radicals, certain other interesting reactive or unstable species have been studied: for example, "red" magnesium and excited electronic states of N_2 and O_2.

Experimental methods of estimating the concentrations of these species are not in satisfactory agreement with each other. The results of electron spin resonance, which presently appear to be the most reliable, indicate a maximum concentration which is of the order of tenths of a (mole) percent. The highest estimate, and also the most suspect, comes from calorimetric studies: this is about 4 percent.

After the experimental methods have been discussed, some theoretical work on concentrations will be mentioned. Several theories have been proposed which predict upper limits to the concentration of radicals that can be trapped. These predictions are in rough agreement with experiment. By judicious choice of a theory one can get more than ten percent or less than a tenth of a percent.

2. General Comments

The experimental techniques which will be discussed are

optical spectroscopy
electron spin resonance
magnetic susceptibility
mass spectrometry

calorimetry
X-ray diffraction
electron diffraction
dielectric constant
index of refraction.

This list shall be gone through to indicate, wherever appropriate, the physical basis for each method, with comments on its utility. But first some general comments, relevant to almost all of these methods, should be made.

Any method of identification is in principle also a method for determining concentration. For example, an extreme lower limit on concentration is always given when the sensitivity of the method is known. Unfortunately, some methods are so sensitive that this lower limit is far from realistic. Emission spectroscopy is an example of this.

Some methods of identification are used very often for analysis; for example, absorption spectroscopy. But here one suffers from standardization troubles. Unless the absorption transition probabilities are known, measurements of absolute absorption intensity are useless. As far as the writer is aware, no one has measured concentrations of the simpler trapped radicals in this way.

Many methods of measuring concentration are useless unless only one reactive species is present, and its identity is known. This is characteristic of magnetic susceptibility studies, and an extreme case is the calorimetric measurement of "heat of recombination".

The effect of the matrix can cause serious troubles in the process of identification. A question which often causes arguments is: what is meant by the "identity" of a species which has been trapped in a matrix? This comes up, for example, in discussions of the difference between a loosely bound $N+N_2$ "molecule" and an N "atom", both contained in a molecular nitrogen matrix. I think that the best answer is the obvious one, that if the effect of the matrix is a small perturbation of the properties of the isolated species ("small" means that only the lowest order in quantum mechanical perturbation theory is needed), then the identity of the isolated species is preserved. If the effect of the matrix is too large to be handled by simple perturbation theory, then the species has not been properly defined, and at least part of the environment must be combined with the original species to make a more complex species.

When a species has been trapped, one should generally expect that its properties will shift in numerical value, and that qualitatively new features can appear. This is particularly true in spectroscopy, but it should be watched for in other techniques. A typical question here is: how much of a shift in frequency is consistent with preservation of identity? In the green glow from the condensed nitrogen discharge, a variety of features appears. It is tempting to settle the conflict between different possible assignments of the spectral lines by picking that assignment which gives the smallest shifts. In the absence of a workable theory of line shifts this is an uncomfortable basis for decision. Another problem in spectroscopy is that transitions which are forbidden to the isolated species can become allowed as a result of interaction with the matrix.

These preceding points, 1. identification can imply concentration;

2. identification is generally required for measurement of concentration; 3. the matrix can have an effect on "identity", should be kept in mind when a particular experimental method is proposed.

3. Optical Spectroscopy

A substantial amount of effort, both at NBS and elsewhere, has gone into the study of the absorption and emission spectra of trapped species. The entire spectrum from the infrared to the vacuum ultraviolet has been spanned. At NBS, infrared spectra have been studied by Harvey, H. Brown (absorption and emission), and Mador, Leifer, Comeford, and Gould (absorption). Visible emission spectra were investigated by Bass, Broida, Hörl, Peyron, Rebbert, and Schoen. Vacuum ultraviolet absorption has been studied by Dressler and Schnepp.

The physical basis of spectroscopic analysis is too well known for further discussion here, but the limitations inherent in this technique deserve discussion. I have already pointed out that the major stumbling-block in measurements of concentration is the lack of information about transition probabilities (or *f*-values). If the trapped species is in weak interaction with its surroundings, and if the transition is strongly allowed in the dipole approximation, one would expect that the *f*-value does not differ much from the gas phase—but this conjecture has to be tested. Also, it is hard enough to get *f*-values for the gas phase. If the interaction with the matrix is strong, or the transition weakly allowed in the gas, then anything can happen.

Optical spectroscopy has been used mainly for identification. If a comparison spectrum of the species in the gas phase is available, and if only a very few, spectrally separated species appear to be present, then identification rests on the reasonableness of frequency shifts. McCarty and Robinson have done outstanding work of this kind. They have supported their identifications by an experimental investigation of the effect on frequency shift of a change in matrix. They have also developed a crude theory of shifts based on empirically known strengths of ground state intermolecular forces. At NBS, Schoen has made a systematic study of the matrix effect, but his data have not yet been theoretically analyzed. There is experimental evidence for shifts not only in the electronic term values but also, in the case of diatomic molecules, in the vibrational frequency and anharmonicity. Each quantum state of a molecule can interact somewhat differently with the environment. This should be a powerful tool for the study of intermolecular forces.

Bass, Broida, Brown, Hörl, Peyron, Rebbert, and Schoen at NBS have investigated the emission spectra from nitrogen which has been passed through a discharge and then condensed at 4° K, or else condensed and then activated by various methods. Their biggest problem is to disentangle the many possible overlapping molecular and atomic transitions, complicated by matrix effects. Here one must depend very strongly on the assumption that shifts are small and systematic. Some of the trouble due to overlapping spectra of different species can be avoided by careful elimination of unwanted material. This is not always easy—for example, Schoen has obtained typical, though weak, nitrogen and oxygen emission spectra from discharged argon containing 10 parts per million of impurity. In many ways it is better to use isotopic substitution; this has been done in the nitrogen problem, and one can be sure that certain lines in the nitrogen spectrum are indeed due to species containing nitrogen. But this device has limited utility.

In summary, optical spectroscopy is not presently useful for absolute determinations of concentration. Its utility for identification is greatest (and in fact it is probably the best method) when a comparison spectrum is available. Until a workable theory of line shifts is developed, the results of optical spectroscopy depend on the assumption that frequency shifts are reasonably small.

4. Electron Spin Resonance

Electron spin resonance (ESR) has become a very popular and quite successful technique for identifying trapped radicals. It has also provided the most reliable data presently available on concentrations of the simpler trapped species. Many laboratories in this country and abroad are using ESR; at NBS it has been used by D. Brown, Florin, Gager, Radford, Wall, and Scheer.

The basic physical effect which is observed by ESR is the interaction of an unpaired electron spin with an external magnetic field. (More precisely, one measures the absorption of microwave energy accompanying transitions between quantum states of the electron in the magnetic field.) Therefore the observation of an ESR signal is evidence that unpaired electrons are present in the sample. By itself, this does not mean that radicals are present. However, there are finer details associated with this gross effect, due to the extra magnetic fields that occur when certain nuclei with magnetic moments are present. In ESR one observes the nuclear spin environment of an unpaired electron spin: this is the basis for identification. If the electron belongs to a molecule, the nuclear spins within the molecule give the biggest environmental contribution, but there are also effects due to the surrounding matrix. If the electron spin belongs, for example, to a nitrogen atom, the fine structure is due entirely to the surroundings. (This is an example of the definition of "identity" which was introduced earlier. The species is properly identified only when the effects of the surrounding matrix are small.)

The nuclear spin environment is seen in two ways. First, it gives rise to a splitting of the free electron ESR spectral line into a number of lines. Second, these lines have different intensities. If the nuclear spin environment is specified, the number of lines and their relative intensities can be predicted theoretically and compared with experiment. Unfortunately the lines are not sharp and their shapes are not precisely known, so that the integrated or total intensities may be hard to get accurately. Another complication, of an experimental sort, is that lines which are broad and weak can be submerged in background noise. Because of this the number of lines can be incorrectly reported.

In spite of these difficulties, ESR measurements in several laboratories have given reasonably conclusive evidence that, for example, hydrogen atoms can be trapped in solid hydrogen, nitrogen atoms in solid nitrogen, and many larger radicals in various rigid matrices.

ESR provides also a method for measuring concentrations of electron spins associated with particular nuclear spin environments. The most serious complication in these measurements appears to be the rather routine one of calibration. Before too long this trouble ought to be eliminated.

At NBS, D. Brown, Florin, and Wall have investigated the concentrations of hydrogen and nitrogen atoms which can be stabilized in a matrix: The atoms are produced by gamma-irradiation. Their results indicate an upper limit to the concentration of the order of a few tenths of a percent. As far as the writer knows, no one has observed appreciably higher percentages of atoms by ESR.

In summary, ESR is a valuable method of observing the nuclear spin environment of unpaired electrons, and hence radicals. In many cases the interpretation of the spectrum is straightforward, and qualitative observations are enough. But interpretations based on relative or absolute intensities are not so safe. More work needs to be done on the shapes of ESR lines in radical-matrix systems, and on the calibration of the equipment at low temperatures.

5. Magnetic Susceptibility

Another method of studying trapped radicals, somewhat like ESR, is measurement of paramagnetic susceptibility. The main work in this field has been done by Barfield, Fontana, and Zahn at NBS.

The magnetic susceptibility of a system is due to its total average magnetic dipole moment. In typical cases this magnetic moment comes from unpaired electron spins. If radicals are present, and there are no other sources of electron spin, this technique can be used to measure concentrations. In the present case it cannot conveniently be used to identify the species present. The susceptibility is directly proportional to the number of spins and inversely proportional to the temperature.

While absolute measurements of the magnetic susceptibility of a system are possible, there are serious experimental difficulties. In systems which have been studied at NBS, the contribution to the susceptibility from radicals is comparable with the contribution from the Pyrex glass of the sample cell. Also, the temperature of the system must be known—any error in temperature is equivalent to an error in concentration.

Fontana has performed some interesting experiments using this technique. He deposited the products of a nitrogen discharge on a helium-cooled surface, and measured the susceptibility and temperature simultaneously as functions of time. He could therefore follow the rate of increase of the number of trapped spins under various conditions, and compare this with the rate of deposit. Also, the gas flow could be stopped, so that the stability of the deposit could be observed. Fontana found that when the gaseous discharge contained more than 1 percent of atoms, no spins could be observed in the deposit. He inferred that the atoms were recombining "instantaneously". But when the concentration of atoms in the gas was of the order of hundredths of a percent, the deposit contained about that many spins and remained fairly stable. Concentrations of the order of a few tenths of a percent could be stabilized for as much as five minutes, but this was the limit of stability at these concentrations. Under these conditions he observed spontaneous "explosions", in which the temperature rose and the spins disappeared rapidly. Of course it is difficult to control and measure temperatures during the deposition of a hot gas, so these results may be quantitatively in error.

To sum up, the technique of paramagnetic susceptibility is capable of giving useful information about concentrations of trapped radicals, but cannot be used for identification in these systems. Great precision is needed, and the temperature must be known with confidence. This method does not appear to be as useful as ESR, especially if the ESR calibration problems can be eliminated.

6. Mass Spectrometry

Mass spectrometry has been used at NBS by Franklin, Herron, Dibeler, and Bradt in an interesting attempt to measure the concentration of trapped nitrogen atoms. A gaseous nitrogen discharge was condensed on a helium-cooled surface, under conditions where it was believed that nitrogen atoms were trapped. The deposit was then allowed to warmup, and the evolved gas was fed into a mass spectrometer. A search was made for nitrogen atoms, but none were observed. The sensitivity of the measurement was such that a hundredth of a percent of those atoms which were believed to be trapped could have been detected. Of course this does not prove that no atoms were present in the solid, since they might have recombined during the evaporation. A positive result would have been more encouraging; but it appears that mass spectrometry is not a valuable technique for measuring concentrations of trapped atoms.

7. Calorimetry

In many fields of chemistry and physics substantial understanding of the properties of materials is gained from thermodynamic measurements. There are, however, both conceptual and practical difficulties in applying calorimetry to systems of reactive species trapped in matrices. The practical difficulties will no doubt be overcome, but we shall have to live with the conceptual ones.

One of the most basic of thermodynamic quantites is heat capacity. A measured amount of heat is added to a system and the consequent increase in temperature is measured. But will such measurements have meaning or utility when trapped *reactive* species are present? The conceptual difficulty here is that the system is not in thermodynamic equilibrium. Species are trapped because their coefficients of diffusion in the matrix are small. When heat is added the temperature increases, the rate of diffusion increases, and the species begin to react. We are dealing with a nonequilibrium process. The specific heat which is measured in this way will generally depend on the rate at which heat is added. Such measurements will, of course, still be interesting; but they are likely to give more information about the kinetics of recombination than about thermodynamic properties.

A conceptually safer kind of calorimetric measurement, which appears to have great value, is that of integral heats of reaction. This should give information about concentrations of trapped species. In a typical experiment, a known amount of heat is allowed to leak into the system. After a while the matrix is warm enough that species can approach each other and react. The evolved heat warms the matrix further, more species react, and so on. Finally the system settles down, and the only subsequent increase in temperature is due to the initial heat leak. If the molar heat of reaction has been determined in some other way, if the specific heat of the pure matrix is known, and if it is assumed that these quantities do not change appreciably when the species is trapped in the matrix, then the initial concentration of reactive species can be obtained.

This kind of experiment was first done by Broida and Lutes. They studied the deposit formed when the products of a nitrogen discharge are condensed on a helium-cooled surface. They could not control the external heat leak (which in fact varies as the vapor pressure of the system changes), so they made similar measurements on the deposit formed from undischarged nitrogen, and used this to determine the external heat input. They estimated that the nitrogen atom content of the matrix was about 0.2 percent.

Minkoff, Scherber, and Gallegher repeated these measurements, after making substantial changes in the calorimeter. These investigators obtained concentrations as high as 4 percent. But considerable doubt may be cast on their results. For example, the nitrogen atom content of the gas in the discharge was determined by entirely different methods to be typically only about 1 or 2 percent. Minkoff and Scherber also observed, using the same equipment, that substantial amounts of heat were released when the condensed products of an argon or krypton discharge were warmed up. Either they were trapping excited atomic states, or some entirely different effect is responsible for their results. Also, Scherber and Fine observed a large evolution of heat when condensed *undischarged* hydrogen was warmed up; and Schoen and Rebbert, by an independent method, observed corresponding thermal anomalies when undischarged hydrogen was deposited. Either something very strange is happening when these gases are condensed on a cold surface or else the experimental technique is not well-suited to this kind of measurement.

Although the calorimetric measurements which have been made are rather discouraging, the idea of determining concentrations from heats of reaction is still very attractive, and more work should be done.

8. X-ray and Electron Diffraction

In this section the techniques of X-ray and electron diffraction will be discussed. Peiser, Bolz, and Mauer have done low-temperature X-ray diffraction studies on a number of the solids which are popular as matrices; and Hörl has studied electron diffraction on solid nitrogen.

In both X-ray and electron diffraction one observes the Fourier transform of the electric charge density in the solid. It should therefore be possible to detect and to measure the concentrations of trapped species. However, it is not likely to be practical unless the trapped species has a considerably higher molecular weight than the matrix molecules.

X-ray diffraction patterns have been obtained for deposits of various condensed gases (argon, nitrogen, oxygen, etc.), both discharged and undischarged. The major difference is that in general the discharged gases produce a more ordered structure. But there is no indication of the presence of atoms in the deposited solids. It appears to be impossible, using the experimental techniques now available, to identify or measure concentrations of the simpler trapped species in matrices.

Hörl has obtained electron diffraction patterns of thin films of nitrogen. Electron bombardment of the solid is known to produce atoms, as shown, for example, by emission spectra. However, the electron diffraction patterns themselves do not show the presence of atoms.

9. Dielectric Properties

N. Brown has investigated the possibility of measuring the dielectric constants of deposited materials, with the hope of observing and determining the concentrations of radicals with electric dipole moments. Dielectric measurements at very low temperatures were found to be unusually difficult. No evidence was observed of any change when a Tesla coil was discharged through solid ammonia.

J. Kruger has studied the index of refraction of thin films of deposited material at low temperatures. In comparisons of discharged and undischarged gases, no systematic differences have been observed. In order to use this method for absolute determination of concentration, one would have to know the polarizability of the trapped species: this is a serious obstacle to precise work, since polarizabilities cannot be estimated reliably for any but the simplest substances.

10. Theoretical Studies

Some theoretical work on trapping of reactive species will be described in this section. Several models have been studied which lead to upper limits on the concentration of species which can be trapped. It is convenient to divide these into static and dynamical theories.

The static models developed by Golden and by Montroll and Jackson depend strongly on the notion of isolation. They assume that if two radicals (e.g., N atoms) are nearest neighbors in a lattice, they will immediately react to give an uninteresting stable species (e.g., N_2 molecules). They also assume that, aside from this nearest neighbor prohibition, the arrangement of radicals and diluent molecules on the lattice is random. The Golden and Montroll-Jackson calculations differ mainly in the details of the statistical analysis. These theories predict maximum concentrations of the order of 10 percent.

The assumption that nearest neighbor radicals will react is certainly plausible. However, it may be too restrictive. (For example, crystalline diphenylpicrylhydrazyl, the most common radical for calibration of ESR equipment, is perfectly stable.) If radicals having parallel spins are nearest neighbors, they will not react unless one of the spins is reversed; and one needs a time dependent perturbation to do this. At very low temperatures the lattice is essentially at rest, and spin-lattice interactions may be quite weak. In this case the radicals can remain unreactive for a long time. At NBS, Windsor performed experiments on the deposition of a beam of spin-alined hydrogen atoms, to see whether the spins would indeed remain parallel in the deposit. Results were inconclusive.

Jackson has proposed a dynamical theory dealing with concentrations of trapped radicals. This theory predicts conditions under which a trapped radical system will be unstable and "explode". In fact his theory shows strong similarities to conventional explosion theory. It is assumed that radicals will occasionally react, as a result of slow diffusion or some external influence. (Therefore the system is not intrinsically stable, though its decay may have a very long lifetime.)

The heat of combination warms the lattice in the neighborhood of the reacting radicals. This heat is dissipated by thermal conduction. (It is conceivable that some other mechanism, for example a shock wave, removes the energy from the reaction region. This point has not been investigated.) Jackson also assumes that there is a critical temperature, such that radicals in a colder region remain trapped, while radicals in a warmer region become "free". By solving the heat conduction problem, one can show that the temperature will rise above the critical temperature only inside a certain volume. If "free" radicals react immediately a chain reaction will ensue whenever the concentration is high enough that more than two radicals are within this volume. By making reasonable guesses about numerical parameters involved in the theory, Jackson obtained critical concentrations of the order of tenths of a percent for nitrogen atoms in solid nitrogen.

Any dynamical theory must remain largely speculative until experimental information is available about mechanisms and rates of reaction of radicals in matrices.

Washington 25, D.C., December 9, 1959.

8. Interactions Between Trapped Species and the Matrix

O. Schnepp [1]

1. Nuclear Degrees of Freedom

The degrees of freedom of a radical or molecule trapped in a matrix are obviously of great importance in the study of such systems. We shall discuss the interactions which determine the extent of translational, vibrational, and rotational freedom in this section.

1.1. Translation

On the basis of available information, there is a striking correlation between the ease of diffusion of a trapped species and the lattice energy of the matrix. By the use of the electron spin resonance technique it has been demonstrated that hydrogen atoms can be stabilized in a matrix of solid hydrogen at 4.2° K, i.e., the diffusion of hydrogen atoms is severely impaired under these conditions [20, 21].[2] Similar observations have been made on atomic hydrogen trapped in solid methane, [21, 43]. For this system it was observed that the resonance spectrum ascribed to atomic hydrogen disappears on slight warming, i.e., below 20° K, indicating that diffusion becomes appreciable. On the other hand, hydrogen atoms have been trapped at 77° K in solid hydrogen acids, concentrated and diluted with ice [45, 23, 22], and in pure ice [26, 40]. In such matrices diffusion only becomes important near 100° K. Similar observations have been made for hydrogen atoms trapped in ammonia [7].

The same matrix will, however, limit the diffusion of different species to a different extent. For example, both hydrogen atoms and methyl radicals have been produced in a methane matrix at 4.2° K but atomic hydrogen disappears on slight warming whereas methyl radicals were observed to survive the same treatment [43]. In another experiment, Smaller and Matheson [39] report that the resonance signal due to methyl in methane decays in a few minutes at 77° K, indicating that the radical has a finite stability at that temperature. A much larger radical, benzyl, has been stabilized at 77° K by Norman and Porter [28] in a glass containing alcohol and ether in addition to a hydrocarbon.

The interactions determining the diffusion rates and activation energies can probably be divided into two parts. The first type is the interaction between the trapped species and the matrix molecules. This is presumably mostly of the van der Waals type in the cases discussed above. It is reasonable that the interaction between a methyl radical and methane molecules should be greater than that between hydrogen atoms and methane, for the same reason that the sublimation energy of solid hydrogen is much smaller than that of solid methane. On the other hand, the comparative stability of hydrogen atoms in ice and in ammonia cannot be understood on the basis of such interactions. It seems that here the binding of the matrix material itself is decisive, leading to a correlation of stability

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[2] Figures in brackets indicate the references at the end of this paper.

of radicals with the binding energy of the matrix lattice. Thus the strongly hydrogen bonded solids may form more rigid cages from which the radical cannot escape at low temperatures. This "cage effect" is then the second type of interaction referred to. There does not seem to be a valid alternate explanation of this stability of free hydrogen atoms in hydrogen bonded media. It does not seem reasonable to invoke hydrogen bonding between free hydrogen atoms and the matrix molecules, as the presently accepted picture of such interactions requires the hydrogen atom involved to be one of the participants in a polar bond.

1.2. Vibration

There is some published evidence concerning the extent of the interactions between trapped species and the matrix as observed in connection with the vibrational degrees of freedom of radicals and molecules. There are two distinct sources of information, the first being from vibrational spectra in the infrared region of the spectrum and the second from the vibrational structure of electronic band systems in the visible and ultraviolet. The latter method of investigation has the advantage of potentially giving information on the deviations of the vibrational quanta from the free molecule values over a wide range of quantum numbers in the ground and excited states.

Infrared investigations have shown that the first vibrational spacing is not appreciably affected by the matrix materials studied, i.e., rare gases and nitrogen, the spectra of the trapped species coinciding with those of the gaseous molecules within a few cm^{-1} [2, 42]. This observation is not unexpected, since the bond energies are very large compared to the binding energies of these solids and presumably the binding energies of the trapped species to the matrix, and since the vibrational amplitudes are small compared to lattice spacings.

Robinson and McCarty [35, 36, 33] have observed the absorption spectrum of NH_2 between 7900 A and 3700 A, and have compared it with the spectrum of the radical in the gaseous state investigated by Ramsay [31, 32]. Twenty quanta of the bending vibration in the excited electronic state of the trapped radical in solid argon have been recorded. The first 10 quanta follow the free molecule pattern very closely but the higher vibrational quanta show a tendency to crowd together in the matrix, as compared to the gas, such that the matrix shift is reported to be 2.5 cm^{-1} to the red for the band corresponding to vibrational quantum number 18, whereas the shift was to the blue by 26.3 cm^{-1} for quantum number 6. The matrix effect on the vibration is here certainly a small one and it is the more difficult to evaluate its significance due to the complexity of the situation in NH_2 introduced by the Renner effect [12]. This term refers to severe anomalies in the vibrational structure due to strong interactions between the bending vibration and electronic motion.

Recently Dressler and Schnepp [13] have observed the Schuman-Runge bands of oxygen, condensed in matrices of nitrogen and of argon, in the spectral range between 1900 A and 1700 A. Discrete but broad bands have been observed between vibrational quantum numbers 4 and 15 in the excited electronic state, followed by a continuum. This system is of particular interest since the equilibrium internuclear distance changes very much from ground state to excited state, namely from 1.21 A to 1.60 A [17]. The vibrational intervals show a slight increase over those of the free molecule. The bands at first seem to converge toward a dissociation limit as in the gas, but about 2,000 cm^{-1} before this limit the bands stop converging and even seem to diverge. This observation is interpreted by the authors as the result of the repulsive forces acting on the oxygen at large internuclear distances due to the surrounding matrix "cage". It is to be noted that the amplitude of the molecular vibrations at this point is twice the ground state internuclear equilibrium distance.

Robinson and McCarty [35, 34] have also reported several vibrational intervals in the electronic spectrum of HNO in an argon matrix. Here the vibrational quanta agree with the gas phase values to within a wavenumber unit.

The Herzberg system of oxygen has been studied by Broida and Peyron [4] and by Schoen and Broida [38] and the Vegard-Kaplan system of nitrogen has been studied by Broida and Peyron [5] and by Schoen and Broida [38] all in emission. These authors have observed long progressions of the ground state vibrations of the molecules and have found the deviations from the free molecule vibrational parameters to be small.

1.3. Rotation

During the last year direct evidence for the occurrence of free or near-free rotation of molecules and radicals in matrices at low temperatures has been presented by various authors. Fine structure in the vibrational absorption bands of water in argon at 20° K has been interpreted by Catalano and Milligan [6] as indicating rotational degrees of freedom. Robinson and McCarty's investigation [35, 36] of the electronic absorption spectra of NH_2 and of NH in argon at 4.2° K has produced excellent evidence that these radicals rotate quite freely in the matrix. They have shown that most of the fine structure of the vibronic bands can be interpreted very satisfactorily if it is assumed that the rotational constants are identical to those observed for the gaseous species. It should also be pointed out that the close similarity between the vibronic structure of the trapped species and that of the gaseous radical can be interpreted as implying that rotation about the axis of smallest moment of inertia is quite free in the matrix. This rotational angular momentum is a factor in the theory of the Renner effect which is the basis of the interpretation of the observed vibronic structure [12]. The recent work by Hexter and Milligan [27], principally on ammonia in matrices, lends further support to the assumption that small molecules have considerable freedom to rotate in solid matrices.

Very recently McConnell [25] has pointed out that the intensity relations among the hyperfine components in the electron spin resonance studies of the NH_2 radical reported by Foner et al. [15] can be interpreted as evidence for free rotation. Foner and coworkers found that the spectrum consists of a hyperfine triplet due to the N^{14} nuclear spin of 1 with every component split into a further triplet due to interaction with the nuclear spin of the 2 protons. The components all have the same intensity. There are two ways of coupling the spins of the protons to give ortho- and para-NH_2 with the proton spins parallel or antiparallel. The para-species cannot reach the lowest rotational state (0_0), being constrained to remain in the 1_{-1} rotational state at low temperatures. This latter level lies 21.11 cm^{-1} above the

0_0 rotational state for the free molecule. If only the ortho-species is present in the matrix at low temperatures the observed intensity relation among the hyperfine structure lines of the spin resonance spectrum can be explained. For this situation to be realized, there must be free conversion between ortho- and para-molecules, such that thermal equilibrium can be established with considerable speed at 4.2° K. The absorption studies of the electronic spectrum of NH_2 indicate that this is indeed the case [35]. McConnell then goes on to argue that the intensity relations in the observed spin resonance spectrum are evidence for the presence of ortho-NH_2 molecules only. Assuming then thermal equilibrium, this indicates that the 1_{-1} state is appreciably higher lying than the 0_0 state or in other words close to the free molecule level, indicating that free rotation exists. If the rotation were seriously hindered in the matrix, the 1_{-1} level would be expected to lie much closer to the 0_0 level, allowing appreciable population of the higher state and therefore an appreciable concentration of para-species. In this case the proton triplets would approach an intensity distribution of 1:2:1. It is thus suggested that such intensity relations in spin resonance spectra are indicative of the degree of hindering of rotation coupled with information on the ease of interconversion between different nuclear spin species.

2. Electronic Interactions

We shall now turn our attention to the effects of the interactions between trapped species and matrix on the electronic transitions of the former. The most intensively studied cases are those of the emission spectra of nitrogen and oxygen atoms in discharged nitrogen deposited on a cold surface at 4.2° K. The studies of these effects are due to Herzfeld and Broida [18] and to Herzfeld [19]. It is demonstrated in these theoretical studies and interpretations of the experimental observations that the highly forbidden atomic transition ^2D-^4S of the nitrogen atom is affected in three ways by the crystal field of the matrix. The ^2D levels are shifted to lower energies by 50 to 100 cm^{-1} relative to the ground state in the solid and they are split by the cubic crystal field. Furthermore, the radiative lifetime of the excited state is reduced by the solid interactions by a factor of 10^3 from the free atom value to about 15 sec in the matrix. The emission spectrum attributed by Broida and Peyron [3] to the transition ^1S-$^1D_2$ of the oxygen atom has been shown [16] to be consistent with the predicted crystal field splitting of this transition into three components, due to the splitting of the D atomic state in the cubic field of the matrix which allows a degree of degeneracy of at most 3.

In recent months spectroscopic investigation of several metal atoms in rare gas matrices have been reported. McCarty and Robinson [24] have observed the absorption spectra of mercury and sodium; Dressler [11] has extended the observations on mercury to the 1849 A line; and Schnepp [37] has studied manganese and magnesium. In all cases the electronic transitions were between S ground states and P excited states, although the multiplicities vary. In all cases, the observed spectra fall close to the free atom spectra and can therefore be correlated with these. It is also true that in all cases groups of three broad lines were observed, although for magnesium and manganese weaker pairs of lines have been observed in addition. It is therefore indicated to conclude that the atoms are located at asymmetric sites in the solid, such that the orbital degeneracy of the excited states is removed wholly or partially. Alternately, the Jahn-Teller effect may be invoked to explain the removal of the degeneracy [24]. Quantitative theoretical analysis is needed before a decision can be made as to which of the two possible interpretations is valid. The observed crystal field splittings are of the order of several hundred wavenumber units and the line widths vary from 20 to 70 cm^{-1}.

Due to the low degree of degeneracy encountered with the electronic states of polyatomic radicals and molecules studied in matrices, crystal field splittings are not observed in these cases. The matrix effects manifest themselves, however, in the observed shifts of the electronic spectra. Robinson and McCarty [35] have discussed the shifts observed for a series of trapped species, namely CH, NH, OH, C_2, NH_2, HNO, NO_2, H_2CO, HCO, and NCO. In the majority of cases a red shift is observed, the largest being that recorded for OH amounting to 395 cm^{-1}. Blue shifts have been observed by these authors for NH_2 (28 cm^{-1}), NO_2 (55 to 70 cm^{-1}), for H_2CO (215 cm^{-1}) and possibly for NCO (70 cm^{-1}). The interpretation of these shifts is very difficult due to the smallness of the effect, amounting in most cases to only a small fraction of the lattice energy of the matrix. It therefore becomes very difficult to divide the observed shift between ground and excited state contributions. Moreover, present day theory of the electronic states of molecules is not capable of predicting with sufficient accuracy small changes in the polarizability of the molecules and radicals accompanying an electronic transition. Robinson and McCarty probably correctly ascribe major importance to this change in connection with the matrix shift problem. They also show that for the same species in different matrices the shift increases with the polarizability of the matrix atoms or molecules. Thus the shift for NH in argon is 195 cm^{-1} while it is 263 cm^{-1} in krypton. The shift for HNO is reported to be 9 cm^{-1} in neon, 54 cm^{-1} in argon, and 68 cm^{-1} in nitrogen. They point out that "the diatomic species (experience) for the most part large red shifts which correspond to an increase of polarizability in the excited state in accordance with the $\pi \leftarrow \sigma$ type of transitions involved." They attribute the considerable blue shift observed for formaldehyde to the marked decrease of the dipole moment in the excited state. This gives rise to stronger binding with the matrix in the ground state than in the excited state.

Recently McCarty and Robinson [24] have presented a quantitative treatment of matrix shifts. They use a Lennard-Jones potential function to represent the interaction between the trapped species and the matrix atoms or molecules and empirically determine the differences in the parameters between ground and excited states. In this way they are able to predict the shift in a third matrix if the data for two matrices are known. Their predictions agree very well with the experimental results in most cases. This work is a very important contribution since it will inevitably further work in the field. On the other hand, the authors point out that their model does not seem to apply to sodium atoms in rare gas matrices. It may be added that the recent results of Dressler [10] for xenon atoms in krypton and argon probably also cannot be accounted for by their scheme. Dressler observed shifts to higher energies of 5,000 cm^{-1} and more for this system. It is certainly correct that the difference in polarizability between the two states will affect the London dispersion forces which play the major role in van der Waals binding. On the other hand, the shifting of charge density from the periphery of a molecule to the interior or vice versa will in many cases seriously affect the energy difference between two electronic states. Such effects have been demonstrated as being mainly responsible for the solvent shifts encountered in cases where hydrogen bonding occurs [30]. In such cases red shifts or blue shifts are observed, depending on the direction of the charge shifts which accompany the electronic transition. Similar considerations should apply in the condensed matrix case but it does not seem clear so far what the criteria are which determine if an attractive or a repulsive effect is to be expected for the electronic interactions between trapped species and the matrix.

3. Electron Spin Interactions

The electron spin resonance spectra of a number of trapped radicals at low temperatures have been reported. Of these the best identified are hydrogen, [7, 21, 22, 23, 45, 26], deuterium, [20, 45, 26], nitrogen, [7, 8, 14, 21, 43, 44], methyl, [21, 39, 43], and NH_2, [15]. Since the spectra of the last two are not known in the gas phase, it is difficult to compare and draw conclusions as to the matrix interaction but the three atomic species have been the subjects of a number of theoretical analyses which give information on this point. A table of hyperfine structure values and *g*-factors of radicals in different matrices is given by Jen et al. [21], and is reproduced here with some additions in table 1.

TABLE 1. *g-factors and hyperfine coupling constants* A *of radicals in various matrices*

Radical	Matrix	g_J	A	Deviation of A from free value	Reference
			Mc/sec	%	
H	free	[a] 2.002256(24)	1420.40573(5)	------------	14
	H_2	2.00230 (8)	1417.11 (20)	−0.23	14
	A	2.00220 (8)	1413.82 (40)	−0.46	14
	CH_4	2.00207 (8)	1411.09 (32)	−0.66	14
	$HClO_4$	2.0022	1407	−0.9	16
	H_2SO_4	2.0024	1415	−0.35	16
	H_3PO_4	2.0024	1423	+0.2	16
D	free	------------	327.3843	------------	13
	D_2	2.00244 (8)	326.60 (23)	−0.24	13
N	free	2.00215 (3)	10.45 (2)	------------	14
	H_2	2.00202 (8)	11.45 (8)	+9.6	14
	N_2	2.00200 (8)	12.08 (12)	+15.6	14
	CH_4	2.00203 (8)	13.54 (22)	+29.5	14
CH_3	free	------------	------------	------------	------------
	H_2	2.00266 (8)	65.07 (13)	------------	14
	N_2	2.00203 (8)	64.64 (20)	------------	14
	CH_4	2.00242 (8)	64.39 (18)	------------	14

[a] Numbers in parentheses following values of g_J and A indicate the last digit accuracies of these quantities where available.

3.1. *g*-factors

The *g*-factors are all in agreement with those obtained from atomic beam experiments within close limits. However, there are very small variations and Jen et al. note that g_J decreases with increasing binding energy of the matrix.

3.2. Hyperfine Structure

The hyperfine structure factors observed for trapped hydrogen and deuterium atoms deviate from the atomic beam value by less than 1 percent except for the case of ice matrices as reported by Smaller et al. [26, 40]. For the most part, the deviations from the free atom values are negative, phosphoric acid matrix being an exception in this respect, the deviation there amounting to +0.2 percent. Very recently Adrian [1] has reported a theoretical calculation of the effect of van der Waals interactions and overlap forces on the hyperfine splitting constant of hydrogen atoms in hydrogen and argon matrices. His results are in good qualitative agreement with the observations.

For nitrogen atoms trapped in inert matrices, the relative deviations of the hyperfine structure constant from the atomic beam value is larger, ranging from 9.6 percent in hydrogen to 29.5 percent in methane, but the absolute deviations are actually smaller. Jen et al. [21] discuss and compare these effects for hydrogen and nitrogen atoms and give a very satisfying qualitative picture on which a successful correlation and perhaps future theoretical work can be based. These authors stipulate that the reason for the negative deviations of the hyperfine structure constant for hydrogen, as opposed to the positive deviations observed for nitrogen atoms can be understood in terms of the difference in the electron density of the free electrons near the nucleus. In the case of hydrogen, the unpaired electron is in a 1*s*-orbital which has high density near the nucleus and therefore has a large h.f.s. constant. Any perturbation which would cause admixture of a higher *p*-orbital would tend to reduce this electron density since a pure *p*-orbital has zero density at the origin. As a result, the h.f.s. constant is here reduced by an external perturbation and the percentage effect will be small since the free atom value is very large. Conversely, in the case of the nitrogen atom, the unpaired electrons are in nearly pure *p*-orbitals and the observed h.f.s. constant for the free atom is very small since it is only different from zero in as much as the unpaired electrons are not pure *p*-orbitals but have slight *s*-character. External perturbations would be expected to increase the admixture of higher *s*-orbitals thus increasing the "spin density" at the nucleus and with it the h.f.s. constant. In this case the effect will be large, percentage-wise since the atomic beam value is very small.

Smaller, Matheson, and Yasaitis [26, 40] have reported observation of an electron spin resonance spectrum characteristic of hydrogen atoms after irradiating ice with γ-radiation. This spectrum consisted of the expected doublet except that the hyperfine separation between them was only $\frac{1}{16}$ that of the free atom. They repeated the experiment with D_2O and observed a triplet, again having a similarly reduced separation. This observation is the only one which deviates from the pattern discussed so far. They propose a model to explain the great reduction in hyperfine splitting constant based on the introduction of an effective dielectric constant. Livingston, Zeldes, and Taylor [23] tried to repeat the experiment and failed. They note, however, that their work on concentrated and dilute acids leads them to believe that in the limit of pure ice, the h.f.s. constant should still be close to the free atom value. These authors seem justified in their criticism of the model proposed by Smaller et al. to explain their anomalous results and until further work is done the observations must be considered as unexplained. The intensity distribution reported by them in their deuterium spectrum is also anomalous. They report a distribution in the triplet of 1:2:1 whereas a ratio of 1:1:1 is expected and observed by other authors, although other observers [21] have reported a more intense center line due to a signal obtained from γ-irradiated quartz.

3.3. Fine Structure

The most elegant chapter to date on the subject of external field perturbations on trapped free radicals has been written by Cole and McConnell [9]. They have treated the crystal field perturbation of a nitrogen atom in a molecular nitrogen crystalline matrix. In zero field they find that the electron spin components of the $^4S_{3/2}$ ground state of the nitrogen atom are split by the crystal field by an amount equal to $2D$ where D is the zero field splitting constant. The two components of electron spin of ½ and $3/2$ are then further split by the magnetic field into two components each. The energies of the four states are also dependent on the angle between the magnetic field and the crystal axes and the analysis of the problem shows that one of the three expected transitions ($s_z=1/2\longleftrightarrow-1/2$) is independent of this angle whereas the other two ($s_z=3/2\longleftrightarrow1/2$ and $s_z=-1/2\longleftrightarrow-3/2$) are orientation dependent. For a polycrystalline assembly it is found then that the first transition will be very intense, since all its intensity is concentrated at one field value. On the other hand the other two transitions will have their intensity smeared out with weak maxima at $\pm D$. Hyperfine coupling with the nucleus of spin 1 leads to the expectation that the spectrum will consist of three intense lines and a weak triplet on either side of them. In fact Cole, Harding, Pellam, and Yost [22] had reported such weak satellites in the electron spin resonance spectrum of nitrogen atoms trapped in a nitrogen matrix, and since then other workers [21, 9] have made the same observation. Actually only four of the six predicted weak lines have been observed, the other two being hidden by the outer pair of the central intense triplet with which they coincide. Cole and McConnell [9] have actually succeeded in demonstrating that the intensity of the outer pair of the central triplet is enhanced relative to the central line due to this coincidence. The zero field splitting parameter D was determined to be 31 ±6 Mc. Wall, Brown, and Florin [44] have observed similar satellites with N^{15}. In an argon matrix, however, they did not observe them and conclude from this that the nitrogen atoms are situated in glassy regions in the matrix. Jen et al. [21] report that the appearance of the satellites depends on the rate of deposition of the matrix, fast deposition leading to their appearance while slow deposition does not. This observation confirms the theory of Cole and McConnell since fast deposition has been observed to lead to higher degree of order in the matrix whereas almost amorphous matrices have been observed on slow deposition at very low temperatures.

The failure to detect some free radicals by electron spin resonance techniques has been suggested to be due to possible crystal field perturbations. Jen et al. [21] propose that it may not have been possible to detect trapped oxygen atoms due to crystal field splitting causing a nondegenerate ground state. They point out, however, that this is only possible in even-numbered electron systems due to Kramer's theorem. This explanation, they continue, cannot be invoked to explain their failure to detect chlorine atoms. It may be that *p*-electrons are very seriously perturbed by a matrix and the resonance spectrum is so broadened as to be undetectable.

3.4. Neighboring Nuclear Spin Interaction

Zeldes and Livingston first reported weak satellites in the spin resonance spectrum of hydrogen atoms in solid acids. They found that the separation of the weak lines from the main features was 35.1 Mc which compares with 36.12 Mc for the proton magnetic resonance as reported in the literature. Zeldes and Livingston [45] therefore proposed that the satellites were due to simultaneous spin flips of neighboring protons, caused by weak magnetic dipole-dipole coupling between the electronic spin of the electron and the nuclear spin of the proton. The intensity ratio between the satellites and the main lines was reported to be about 1:35 and this value could be fitted to a rough theory to give a distance to the neighboring proton. This theory has been refined by Trammell, Zeldes, and Livingston [41] and the distance calculated from the intensity ratio was 1.8 A, a very reasonable value. These authors also give generally applicable formulas for similar events involving other systems. Livingston, Zeldes, and Taylor [22] point out that the hydrogen atom must be at rest in order for the phenomenon to be observed. This is therefore the only really direct evidence for impeded diffusion of a free radical in a matrix. Jen et al. [21] report two pairs of weak satellites in the electron resonance spectrum of atomic deuterium in deuterium molecular crystal matrix and one pair as discussed above for atomic hydrogen in solid molecular hydrogen crystal. The second pair has a separation from the main line of exactly twice that of the first pair and has been interpreted as representing a simultaneous deuteron nuclear spin transition of $\Delta M_I=2$ induced by quadrupole coupling arising from the quadrupole moment of the deuteron. These authors also discuss the possibility of a spin flip of one proton in view of the fact that this would result in the conversion of an ortho-hydrogen to a para-hydrogen or vice versa. They conclude that this is not likely and believe that the electron spin transition could cause both protons of an ortho-hydrogen to undergo spin flips. Their scheme is not clear, however, and the problem they raise cannot be considered to have been solved satisfactorily.

3.5. Line Width

The line widths of electron spin resonance spectra of free radicals in matrices has not been treated in any detail. It is possible that this parameter could give information concerning the interactions of the trapped species with the environment. Smaller, Matheson, and Yasaitis [40] have interpreted their observed line widths for hydrogen and deuterium in terms of interaction with neighboring nuclei. Jen et al. [21] have discussed line width in terms of a number of parameters and conclude that it is mainly due to anisotropic broadening in the polycrystalline assembly of which they believe their matrices to consist.

4. Nuclear Spin Species Conversion

It seems worth while to add a word about nuclear spin conversion at low temperatures, since this process may depend on interaction with paramagnetic species in the environment. It has been shown that conversion does take place allowing thermal equilibrium to be established at low temperatures with remarkable efficiency in NH_2 trapped in a matrix [35]. On the other hand, this does not seem to be so for the methyl radical. The intensities of the hyperfine components in the electron spin resonance have been observed to be in the ratio 1:3:3:1 [21, 39, 43] and they would be predicted to be of equal intensity if only one nuclear spin species were present. McConnell [25] has, however, suggested that serious hindering of the rotation could be responsible for this result. The problem of interconversion between different nuclear spin species of molecules is a very basic one and deserves serious attention. It is also possible that the efficient interconversion observed for NH_2 is caused by intramolecular effects such as the presence of the nuclear spin of the nitrogen nucleus.

The author acknowledges many stimulating and illuminating discussions with Dr. K. Dressler in the course of the preparation of this review and also is indebted to Drs. J. L. Franklin and H. P. Broida for allowing the use of their, as yet unpublished, review paper.

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WASHINGTON 25, D.C., November 18, 1959.

9. Summary of the Fourth International Symposium on Free Radical Stabilization

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1. Introduction

The Fourth International Symposium on Free Radical Stabilization, sponsored by the National Bureau of Standards, was held in Washington, D.C., from August 31 to September 2, 1959 at Dunbarton College. The first of the Symposia on Free Radicals took place in 1956 and was organized by Professor P. A. Giguère of Laval University, Quebec. It was apparent that there was considerable interest in the general topic of free radicals and a second symposium was held at the National Bureau of Standards in Washington, D.C., in September 1957. By that time, a 3-year program on the stabilization of free radicals, sponsored by the Department of Defense,had been instituted under the direction of Dr. H. P. Broida. Following in the now established tradition, Professor G. Porter arranged for a Faraday Society informal discussion on free radical stabilization early in September 1958 at Sheffield University in England. The decision to hold the fourth symposium in Washington, D.C., was largely based on the fact that the Free Radical Program at the National Bureau of Standards was scheduled to end in September 1959 after running its term of 3 years. Holding the meeting in Washington would then give overseas visitors and other visitors the opportunity to inspect the research taking place in the program prior to its termination. The decision was made to hold the fifth symposium at Uppsala, Sweden in July 1961.

The title of the Fourth Symposium was "Trapped Radicals at Low Temperatures". The number of papers (29) in no way reflected the very considerable growth of interest in the subject over the past 3 years. To prevent the program from becoming unwieldy and to maximize the participation of workers outside the National Bureau of Standards, no papers had been accepted from members of the National Bureau of Standards program. Instead, their work was described in several survey papers. Two such papers were devoted to surveying respectively the experimental and the theoretical aspects of the National Bureau of Standards program. The other survey papers, while placing emphasis on a review of work done at the National Bureau of Standards, had a somewhat broader scope and attempted to define the state of accomplishment in a number of areas which also served as the theme for each session. These were as follows:

(1) Low-Temperature Chemistry;
(2) Methods of Production of Trapped Radicals, and Physical Properties of Radical-trapping Solids;
(3) Identity and Concentrations of Trapped Radicals; and
(4) Interactions of Free Radicals with Solids.

In addition to the survey papers, 22 contributed papers, grouped under the general headings given above, were presented plus 6 five-minute papers describing recent work.

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[1] Guest scientist from Space Technology Laboratories.

Except for the surveys, which were allotted 30 min, each author was given 10 minutes to highlight the important points made in his paper. The success of a symposium may be measured largely by the amount of discussion that takes place. This depends quite crucially on the amount of time available for discussion. The various session chairmen deserve the utmost praise for keeping the meeting on schedule.

For those interested in statistics, the distribution of papers by (a) author's country, and (b) the techniques used are given in tables 1 and 2. In all there was a total of 318 registrants from 12 countries.

In addition to the technical sessions, a round table discussion was held on "Future Trends in Trapped Radicals Research". Giguère (Laval University) presided over a panel comprised of: Fernandez-Moran (Massachusetts General Hospital); Pimentel (University of California, Berkeley); Rice (Catholic University); Broida (National Bureau of Standards); and Porter (Sheffield University). There was also a program of sightseeing for the ladies and a symposium banquet. The guest speaker at the banquet was Mr. Lewis Strauss who, in an address entitled "A Lilliputian in Laputa", reminisced on his past association with such scientific giants as Albert Einstein, Enrico Fermi, Ernest Lawrence, Leo Szilard, and John von Neumann.

TABLE 1. *Distribution of papers by country (including 5-min papers).*

Canada	2
France	2
Israel	1
Sweden	1
UK	4
USA	22
USSR	2

TABLE 2. *Distribution of papers among techniques used*

Liquid nitrogen temperatures	15
Liquid helium temperatures	9
Electron spin resonance	10
UV spectroscopy	5
IR spectroscopy	3
Thermometric and calorimetric	3
Microwave discharge	3
UV photolysis	8
X-rays	1
γ-rays	6
Atomic beams	1
Strong magnetic fields	2

An exhibition of glass and metal Dewars developed during the National Bureau of Standards program was arranged by Hofman Laboratories and by H. S. Martin Company, and a display of publications was put on by the National Bureau of Standards. Also attracting attention were the galley proofs of a much anticipated book, *The Formation and Trapping of Free Radicals*, to be published shortly by Academic Press, edited by Bass and Broida, with chapters contributed by several members of the Free Radicals Program, and ranging in scope from fundamentals to the importance of trapped radicals in astrophysics, biology, and propulsion.

2. Flavor of the Symposium

Seen in overview, this year's symposium had a decidedly more fundamental flavor than those held in previous years. This was reflected by the decreased number of participants from industry compared to universities and government laboratories. In particular, there was only passing mention of trapped radicals in the fields of astronomy, biology and rocket fuels, all three of which had papers devoted to them at earlier meetings. It has become apparent since then that, discounting the possibility of radically new discoveries, trapped free radicals are not the answer to the missile-man's prayer. One cannot blame the rocketeers for being disenchanted by the prospects of harnessing the energy (all 1 kcal/mole of it) of a fraction of a percent of nitrogen or hydrogen atoms trapped in a solid which has to be kept at liquid helium temperatures. In the fields of astronomy and biology probably all has been said that can safely be said and perhaps a trifle more at the present state of our knowledge.

The dramatic blossoming of the free radicals field has now faded, but the seeds of interest have been widely disseminated. Those who came to admire only the flower have gone home again but those whose interest is more deeply rooted are waiting to see what the seeds will produce. This is all to the good. The study of free radicals and unstable chemical species is a fascinating subject and has been so for a devoted few for a number of decades.

3. The Technical Sessions

3.1. Session A: The National Bureau of Standards Free Radicals Research Program

Chairman: R. D. Huntoon (National Bureau of Standards)

(1) Organization and Rationale of the Free Radicals Program—J. W. Moyer (General Electric Company, Santa Barbara, Calif.).

(2) The Experimental Aspects of the National Bureau of Standards Free Radicals Research Program—M. D. Scheer (National Bureau of Standards).

(3) A Survey of the Theoretical Work on Trapped Radicals at the National Bureau of Standards—C. M. Herzfeld (National Bureau of Standards).

This session was devoted to reviewing the National Bureau of Standards program. Moyer (General Electric Company) covered the organization and rationale of the program; Scheer (National Bureau of Standards) covered the experimental research program; and Herzfeld (National Bureau of Standards) covered the theoretical aspects of the program. Moyer described how the National Bureau of Standards Free Radicals Program was conceived as an experiment in research management in which about 30 senior scientists of proven ability would be gathered together and allowed to determine their own research program. Red tape was cut to a minimum and a horizontal-type organization of staff itself reduced formality and encouraged collaboration and interchange of ideas. By such means it was hoped to produce a creative and stimulating atmosphere with few constraints—an environment which should keep a varied group of scientists happy and imbued with a high morale. Participants were drawn from industrial organizations and from universities, both here and abroad. The National Bureau of Standards was chosen as the site for the program because of the unique facilities it had to offer in the way of physical plant, services, and supply of liquid helium, and the "neutral" atmosphere favorable to industrial participation. The program was directed by Dr. Broida as section chief and Dr. Bass as assistant chief.

Those responsible are to be congratulated on foreseeing that the major purpose of a program such as this was not to produce exotic propellants, nor yet even to make studies of their feasibility, but rather to pioneer the opening up of an exciting and provocative frontier of science. The major product of the National Bureau of Standards Free Radicals Research Program, underlined by the more than 100 research papers produced, has been knowledge—knowledge of how to make free radicals, knowledge of the conditions under which they may be stored, of their identity, their concentrations, their properties and their reactions, and finally and perhaps most important of all, knowledge of how to do chemistry at temperatures close to the absolute zero of temperature. And in addition to knowledge has come also a host of new questions, new problems, and new ideas. And that is as it should be.

In his review of the experimental program, Scheer (National Bureau of Standards) said that 0.1 percent appears to be a typical figure for the maximum concentration of radicals that can be stabilized at low temperatures. Larger amounts are very unlikely.

Of the various processes involved in the production and stabilization of free radicals, probably the most complex and least understood is the process of deposition. Except for the recent studies of Baurer, Foner and Mauer, and Windsor, little work has been done in this area. From this work one concludes that large differences in temperature can exist between the cold substrate and the growing surface of the deposit, especially when the solid is disordered by the presence of atoms, radicals or foreign molecules and has in consequence a thermal conductivity several thousand times less than that of the perfect crystal. The true temperature of deposition thus becomes, by reason of the drastically lowered conductivity, a very sensitive function of the flow rate.

The experiments of Schoen, Schnepp, and Dressler were cited on the perturbations of atomic and molecular spectra caused by various matrices and the useful information about the local environment to which this can lead.

According to Scheer, the following areas deserve increased attention in the future:

(1) Deposition process,
(2) Low temperature chemistry,
(3) Interaction of trapped species with the matrix,
(4) Kinetics of crystallographic changes at very low temperatures.

Herzfeld (National Bureau of Standards) praised the close interaction between experimentalists and theorists within the Free Radical Program. He highlighted the following topics: deposition, emission and absorption of energy, and disappearance of free radicals. The common weakness of all the deposition theories is that they ignore temperature gradients and diffusion. The statistical theories lead to predicted trapped concentrations between 5 and 17 percent depending on the coordination number. These are all upper limits. The comparison with experiments is not good—maximum concentrations experimentally observed being of the order of a few hundredths of 1 percent. Jackson's dynamic theory comes closer to experimental reality in predicting a maximum stable concentration of the order of 0.7 percent.

In the field of spectroscopy, considerable success has been obtained in accounting for the nitrogen afterglow. The mechanism by which the excited atoms are produced is still poorly understood. Herzfeld concluded that the two most important new fields are:

(1) The theory of chemical condensation,
(2) The photochemistry of solids.

3.2. Session B: Low-Temperature Chemistry

Chairman: G. Porter (Sheffield University)

(1) Hydrogen Atom Reactions with Toluene—R. B. Ingalls (Atomics International).
(2) Low-Temperature Irradiation of Mixtures of HBr and C_2H_4—D. A. Armstrong and J. W. T. Spinks (University of Saskatchewan).
(3) Radical Reactions at Low Temperatures as Studied by ESR—M. Fujimoto, D. J. E. Ingram, and M. C. Saxena (University of Southampton, England).
(4) Kinetic Studies of the Disappearance of Hydroxyl Radicals in Ice at Low Temperatures—J. M. Flournoy, L. H. Baum, S. Siegel, and S. Skolnik (Aerojet-General Corporation).
(5) Free Radical Conversions in Solids—V. V. Voevodsky (Academy of Sciences, Moscow).
(6) Review: Low-Temperature Chemistry—R. Klein (Olin-Mathieson Chemical Corporation and National Bureau of Standards).

Low-temperature chemistry is the study of chemical reactions below an arbitrarily specified temperature of 150° K. Below this temperature, only reactions with activation energies of a few kilocalories per mole or less proceed at a measurable rate. This simplifies the system by greatly restricting the class of possible reactions. Also, small differences in activation energy will cause measurable changes in observed rates. The disadvantage is that the processes of escape from the solvent cage and diffusion through the solvent may well become rate controlling steps. Klein (Olin-Mathieson) and Scheer (National Bureau of Standards) deserve praise for opening up this field by their studies of H-atom addition reactions to solid olefins in the region of 77° K. Ingalls (Atomics International) described similar work in which he studied the addition and abstraction reactions between deuterium atoms and *liquid* toluene between $-88°$ and $-79°$ C.

Another way of initiating chemical reactions at low temperatures is by gamma-irradiation of a mixture. This was done by Armstrong and Spinks (University of Saskatchewan) who studied the addition of HBr to C_2H_4 both in the liquid just above its melting point at $-165°$ C and in the solid at $-196°$ C.

Fujimoto, Ingram, and Saxena (Southampton University) photolyzed H_2O_2 in hydrocarbon glasses at 77° K and attributed the observed changes in ESR spectra to reactions of OH radicals with the substrate to produce secondary radicals. In the case of OH radicals produced in ice by gamma-irradiation, Flournoy, Baum, Siegel, and Skolnik (Aerojet-General Corporation) found that the rate determining process for disappearance of the ESR spectrum was migration of the radicals through the ice.

In the ensuing discussion there was controversy over the assignment of the ESR spectrum to the OH radical. Both Livingston (Oak Ridge) and Foner (APL) stated that in polycrystalline specimens, crystal anisotropy would smear out the spectrum, and that an unambiguous assignment could be made only by careful work using single crystals.

The "cage" effect came in for considerable discussion. Pimentel (University of California, Berkeley) believed that for methyl radicals at 20° K in a CD_4 matrix, energies of 3 or 4 times the activation energy for D atom abstraction were necessary to overcome the cage effect. However, McNesby (National Bureau of Standards) pointed out that this could be accounted for by the ambiguities in the magnitude of the activation energy and by a reasonably large steric factor. In addition, Willard (University of Wisconsin) and Cochran (APL) presented evidence for decreased quantum yields in glassy solids at low temperatures which they attributed to the cage effect.

To sum up, it appears that, while hydrogen atoms can readily diffuse through a solid film at 77° K, for larger radicals, such as iodine atoms or methyl and ethyl radicals, the process of escape from the solvent cage and diffusion through the solvent environment may well become rate controlling.

In the field of techniques, Thomas (Shell Research Ltd. and National Bureau of Standards) has developed a rotating Dewar for use at liquid helium temperatures. By depositing two reactants on the rotating drum from jets on opposite sides of the cylinder, a kind of helical sandwich roll can be built up. It is hoped that in this way secondary reactions between the reactants can be largely prevented The Low-Temperature Chemistry Session ended with a survey paper by Klein (Olin-Mathieson and National Bureau of Standards) which summarized National Bureau of Standards work in this field.

3.3. Session C: Methods of Production of Trapped Radicals and Physical Properties of Radical Trapping Solids

Chairmen: R. C. Herman (General Motors Corp.)
S. Claesson (Uppsala University, Sweden)

(1) Studies of Some New Matrices for Radical Stabilization—H. T. J. Chilton and G. Porter (University of Sheffield, England).
(2) A Calorimetric Study of Trapped Radicals Produced by Gamma Radiation—R. L. Arnett, E. D. Guth and J. R. Berreth (Phillips Petroleum Company, Bartlesville, Oklahoma).
(3) Photolysis of Chromate, Permanganate, and Related Compounds in Rigid Media at Low Temperatures—U. Kläning and M. C. R. Symons (University of Southampton, England).
(4) High Resolution Infrared Spectroscopy of Solids: Intermolecular Interactions in the Solid State; Extent of Freedom of Rotational Motion of Small Molecules in Inert Gas Matrices—R. M. Hexter and D. Milligan (Mellon Institute, Pittsburgh).
(5) Atomic-Beam Studies on the Formation of Free-Radical Solids—R. T. Brackmann and W. L. Fite (General Atomics, La Jolla, California).
(6) Review: Methods of Production of Trapped Radicals and

Properties of Radical-Trapping Solids—A. Thomas (Shell Research, Chester, England, and National Bureau of Standards).

In the past few years it has become apparent that the physical properties of the matrices used for trapping radicals are extremely important. This includes not only such obvious factors as rigidity and chemical inertness but less obvious ones such as specific crystalline structure, thermal conductivity, molecular weight, and the velocity of sound in the matrix materials.

Porter and Chilton (Sheffield University) described a novel attempt to stabilize aromatic radicals in a matrix of KCl. The work was done at about −110° C and only fairly stable radicals such as diphenyl methyl could be trapped. It appears that trapping occurs actually in microcrystals of the solute rather than in the matrix itself.

Arnett (Phillips Petroleum) described calorimetric work on gamma-irradiated samples of ammonia, argon, and nitrogen at 4.2° K. Measurements showed that only a few percent of the energy put in by gamma-irradiation was stored in the solid. He confirmed the curious effect noted earlier by other workers in the field that stored energy was found to be released at temperatures below that at which it was stored.

Kläning and Symons (Southampton University) described the photolysis of anions, such as permanganate, in alcohol solvents at 77° K. The observed reaction leads to tervalent manganese and oxygen and they believe that the primary step involves four electrons and the extrusion of a molecule of O_2.

By observing the changes in high resolution infrared spectra of small molecules, such as H_2O, NH_3, and CH_4, in rare gas matrices at 4° K, Hexter and Milligan (Mellon Institute) have obtained information on the freedom of rotational motion in rare gas matrices at 4.2° K.

Brackmann and Fite (General Atomic) described experiments on trapping hydrogen atoms at liquid helium temperatures using an atomic beam technique. With a beam of intensity 10^{14} to 10^{16} particles per second, no evidence was obtained of stabilization of atoms even when a spin-alined beam was used. However, at flow rates of about 10^{18} particles per second, periodic energy releases during the condensation of hydrogen occurred. Later experiments showed that considerable reflection of a mixture of H atoms and H_2 molecules occurred from a surface even at temperatures as low as 2.2° K.

During the discussion of the effects of the matrix on the trapped molecule, Dressler (National Bureau of Standards) described a spectroscopic observation of the cage effect, in which changes in the Schumann-Runge absorption bands of oxygen are observed in an argon matrix. The importance of the thermal conductivity of the matrix was emphasized by both Windsor and Herzfeld who agreed that at liquid helium temperatures the disorder introduced in a lattice by the presence of trapped atoms and radicals could well reduce the thermal conductivity by several orders of magnitude due to the scattering of phonons that would take place. Windsor described experiments similar to those of Brackmann and Fite in which energy pulses and pressure pulses had been observed during the deposition of discharged streams of hydrogen, deuterium, and nitrogen. He emphasized that the temperature of the growing surface of a deposit may be several degrees above that of the substrate and attributed the temperature pulses to the periodic recombination of atoms which took place when the growing surface of the disordered deposit reached a critical temperature. In the case of molecular hydrogen the observed temperature pulses are attributable to a small amount of water vapor impurity.

It was generally agreed that we need to know much more about the physical properties of the matrices used for trapping atoms and free radicals. Fortunately, studies of the effects of the surrounding molecules on the spectra of trapped atoms and radicals provide us with a powerful tool for learning about the structure of the matrix.

3.4. Session D: Identity and Concentrations of Trapped Radicals

Chairman: G. Pimentel (University of California)

(1) ESR Spectra of Trapped Radicals Produced by Photolysis of Group IV and V Hydrides—E. L. Cochran (Applied Physics Laboratory, Silver Spring, Maryland).

(2) Isolation and Identification of New Oxides of Nitrogen—H. A. Bent (University of Minnesota).

(3) Free Radicals in Organic Solids—R. L. McCarthy, R. G. Bennett, E. J. Burrell (E. I. DuPont de Nemours, Inc., Wilmington, Delaware).

(4) Electron Spin Resonance Spectroscopy of Radicals Formed by X-irradiation of Amino Acids and Related Compounds—C. A. McDowell and A. J. Horsfield (University of British Columbia).

(5) Experiences with Sulfur Radicals Trapped at 77° K—S. Sunner (University of Lund, Sweden).

(6) Survey of the Status of Research on Identity and Concentrations of Trapped Radicals—R. Zwanzig (National Bureau of Standards).

Spin resonance played a large part in the work described at this session. Cochran (APL) described experiments in which hydrides of carbon, silicon, nitrogen, and phosphorus were photolyzed at high dilutions in an argon matrix. There does not seem to be much doubt about the assignment of the spectra of the simpler radicals such as CH_3, CD_3, and SiH_3. The spectrum obtained for SiH_3 is identical with an earlier unknown spectrum obtained by many workers with an electrical discharge in hydrogen, thus confirming the idea that silane was being formed in small amounts by the reaction of hydrogen atoms with the glass or quartz walls of the discharge tube. Burrell (DuPont) described the observation of free radicals produced by gamma-irradiation of organic solids. The importance of using single crystals in ESR work was emphasized by McDowell and Horsfield (University of British Columbia) who described experiments on the X-irradiation of amino acids and related compounds. The complex spectra obtained were strongly dependent on the crystal orientation. They concur with the interpretation of Ghosh and Whiffen that the observed spectra are probably due to NH_3^+, $CH_2CO_2^-$.

In addition to radicals, thermodynamically unstable new forms of molecules may often be trapped in films frozen at 4.2° K. Bent (University of Minnesota) has evidence for several new oxides of nitrogen from infrared studies. The spectra of the frozen oxides were very sensitive to choice of matrix and dilution ratio, window temperature and the rate of deposition. Self matrices and matrices of argon, nitrogen, oxygen, carbon dioxide, nitrous oxide, and hydrogen were used. In the case of NO_2 at high dilution the spectrum of the monomer is obtained. However, during warmup dimerization occurs and several forms of the dimer have been isolated.

Sunner (University of Lund, Sweden) described attempts to measure recombination energies of organic radicals trapped in an organic matrix at 77° K. Aliphatic disulphides were chosen and the radicals were produced by photolysis. A new absorption band attributable to the thiyl radical was observed and at the same time the disulphide spectrum decreased in intensity. However, the primary reaction products appeared to react with the matrix material (mixtures of 3-methyl pentane or methyl cyclohexane in six parts of isopentane) even at 77° K.

During the discussion, several people emphasized that the very sensitivity of the spin resonance technique brings with it a considerable lack of specificity and ambiguity in assignment. In addition to single crystal studies, therefore, gross chemical analysis by standard techniques of samples studied by spin resonance is to be strongly recommended.

In his review of this field, Zwanzig (National Bureau of Standards) discussed the various techniques which have been used for the indentification of trapped radicals and for estimating their concentration. Warmup and heat release experiments agree with ESR in giving concentrations of a few tenths of a percent. Fontana obtained a similar figure for nitrogen atoms by a magnetic susceptibility method.

3.5. Session E: Interactions of Free Radicals with Solids

Chairmen: R. Livingston (Oak Ridge National Laboratory)
N. Kurti (Oxford University)

(1) Multiple Trapping Sites for Hydrogen Atoms in Various Matrices—S. N. Foner (Applied Physics Laboratory, Silver Spring, Maryland).
(2) Interconversions of Ions and Radicals in Radiolysis—V. L. Tal'rose and E. L. Frankevitch (Academy of Sciences, Moscow).
(3) Intermolecular Interactions of Trapped Species with the Solid at 4.2° K—M. McCarty, Jr., and G. W. Robinson (Johns Hopkins University).
(4) Isothermal Decay of the α (5229 A)—Radiation from Trapped Nitrogen Atoms—R. A. Hemstreet and J. R. Hamilton (Linde Company, Tonawanda, New York).
(5) Magnetic Interactions of Free Radicals at Very Low Temperatures and in Strong Magnetic Fields—W. E. Henry (U.S. Naval Research Laboratory, Washington, D.C.).
(6) Review: The Interactions between Trapped Species and the Matrix—O. Schnepp (Israel Institute of Technology and National Bureau of Standards).
(7) Summary of the Symposium—M. W. Windsor (Space Technology Laboratories, and National Bureau of Standards).

By studying the interactions of free radicals with their molecular environment, one can get information about the structure of the matrix. Foner (APL) described ESR experiments on hydrogen atoms trapped in various rare gas matrices at liquid helium temperatures. Perturbations produced by the matrix cause deviations of the hyperfine coupling constant and the electronic *g*-factor from the free atom value. H-atoms could either be deposited from a discharge or produced photolytically in *situ.* The spectra for *deposited* H-atoms could be explained in terms of a single site which is probably a substitional site. These same sites plus additional ones also are found in the photolytic experiments. These may be attributable to interstitial sites, but owing to lattice distortion the effect on the hyperfine spectrum is difficult to calculate. In the case of xenon an additional splitting occurs caused by the magnetic moment of the xenon nucleus.

Pertubations by the matrix also affect the electronic spectra of trapped species. McCarty and Robinson (John Hopkins University) observed shifts in the electronic absorption spectra of Hg, NH, and C_2 in rare gas crystals at 4° K. These are explained quantitatively on the basis of a Lennard-Jones potential between the trapped species and the rare gas atoms. Good agreement is obtained except in cases where strong angular dependent forces differing appreciably in the two electronic states are present. Later, Schnepp (Israel Institute of Technology and National Bureau of Standards) reported similar experiments with manganese and magnesium atoms in matrices of argon, krypton, and xenon. Although the spectra obtained lie close to those of the gas-phase in energy, the splitting of orbital degeneracies indicates a high degree of asymmetry in the atomic environment.

Hemstreet and Hamilton (Linde Company) have measured the decay rates of the alpha lines of the nitrogen atom afterglow in the range 4° to 30° K. If the temperature be raised in a step-wise fashion, each increase in temperature causes an increase in glow intensity followed by a decay at constant temperature. The glow may be continually restimulated by raising the temperature and even at 30° K active species still remain trapped, as indicated by the intense green glow observed when the temperature was raised at the end of each run. The initial decay rate increases with temperature. After about 10 min., all the curves tail off to an approximately equal rate. Much discussion on the nitrogen afterglow followed this paper and it was apparent that although the observed spectra correlate well with known emissions of atomic nitrogen, the mechanism by which the excited atoms are produced in the solid is still very poorly understood. The two main mechanisms are:

(1) Excited nitrogen atoms are trapped during the deposition process. These have a very long lifetime, perhaps longer than 20 hr. During warmup they diffuse to radiative sites. It transpired that the experiment which might settle this point, namely the storage of a sample for a period much longer than 20 hr, had never been done.

(2) Excited atoms are produced during the recombination process, the energy of recombination of two ground state atoms serving to raise a third atom to an excited state. To test this mechanism it seems important to know not only the spectrum of the afterglow but also the spectrum of the flashes which occur during deposition and during warmup and also the lifetime of the light emission from the flashes. It is apparent from Hemstreet's work that the nitrogen atoms trapped in the solid cover a range of energies. Windsor (Space Technology Laboratories and National Bureau of Standards) and Hemstreet (Linde Company) both reported observations of quasi-periodic temperature pulses which are coincident with the light flashes during the deposition of discharged nitrogen.

Henry (U.S. Naval Research Laboratory) described an investigation of the magnetization of the free radical diphenyl-picryl hydrazyl (DPPH) in magnetic fields up to 60,000 gauss and at temperatures in the liquid helium range. Pressures of 10,000 lb/in.^{2} appeared to increase the magnetic interaction and may possibly cause recombination of free radicals.

Leach (Laboratory of Chemical Physics, Paris) discussed the effect of rigid media on photochemical processes in the benzene molecule. Owing to the high symmetry of benzene there may be qualitative changes in the rigid media due to the effects of external perturbations on the effective symmetry of the molecule.

In his survey paper on the interactions between trapped species and the matrix, Schnepp discussed the effect of matrix perturbations on the various molecular degrees of freedom.

The symposium ended with a summary by Windsor (Space Technology Laboratories).

4. Summing Up

The subject of free radical stabilization at low temperatures has outgrown the excesses of adolescence and has now reached the fruitful stage of maturity. Stimulated by the 3-year program at the National Bureau of Standards, research activity in the field of free radicals will almost certainly continue to increase in the future. In addition to the research that has been accomplished, much else of importance has also been gained, especially in the fields of arts and techniques, due in large part to the fine efforts of Stober (National Bureau of Standards). A large array of experimental Dewars, both metal and glass, has been developed at the National Bureau of Standards and many of these are now available commercially.

Up to the present, and this is quite apparent from a cursory examination of the program of the symposium, most of the work at liquid helium temperatures has been carried out in the United States. This is because of the abundant supply of helium from natural sources in this country and the paucity of such supply abroad, most of what is available being jealously guarded by the low temperature physicists. However, this situation looks as if it will be remedied in the near future and we can then expect a worldwide increase in chemical experiments in the liquid helium temperature range.

5. The Future

The following is one man's opinion of those areas most deserving of our attention in the future in the field of free radicals research at low temperatures.

5.1. Mechanism of Deposition and Condensation

The processes occurring when a gas at 300° K condenses on a surface held at 4° K are very poorly understood theoretically, and there is virtually no experimental information available. It is apparent that the thermal diffusivity of the deposited solids will play a crucial role, since it will largely determine the temperature gradient existing between the liquid helium-cooled substrate and the growing surface of the deposit which is in thermal contact with the incoming gas stream. If the temperature gradient is large, the true temperature of the growing surface may be many degrees above that of the substrate. The structure and degree of disorder of the condensed solid will therefore be a function of many variables, including the gas flow-rate, the gas temperature, the heat of condensation, the thermal diffusivity of the portion of deposit which has already condensed and the thickness of that deposit. And in turn the thermal properties of the deposit will depend crucially upon the degree of disorder. We thus have to contend with a nonlinear and highly complex system.

5.2. The Structure of Solids

Before we can properly understand the properties of solids relevant to the trapping of free radicals and their subsequent recombination during warmup, we must increase our understanding of the matrix itself. Strangely enough the study of trapped radicals themselves promises to give the answers to many of these questions. By using a trapped radical as a probe and observing the effects of the molecular environment on the energy levels of the radical, as observed by all branches of spectroscopy from the infrared to the ultraviolet and by spin resonance, much information can be gained about the structure of the matrix.

5.3. Low-Temperature Chemistry

This is a field so far largely unexploited. In the gas phase at room temperatures few reactions are simple, most proceeding by a complicated series of steps. At low temperatures and in rigid matrices many of the secondary reactions are prevented and it becomes possible to study the kinetics of primary processes and measure their energies of activation. It is also apparent that besides free radicals, thermodynamically unstable new forms of otherwise stable molecules may be trapped at low temperatures. Besides the intrinsic interest of such species from the point of view of molecular architecture and bond energies, there is real hope that the use of low temperatures may enable the industrial chemist to gain a very nice control of chemical reactions. Low-temperature chemistry may well mark the beginning of a new era of precision in chemical synthesis.

Washington 25, D. C., December 16, 1959.

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