750 megacycles Venus looks like a black body of about 450°K, and at Arecibo the radio spectrum is being extended downward to 430 megacycles where the temperature is 200 or 300 degrees. Interesting properties of both planets are being revealed by the radio observations, and it is clear that the dominant radio characteristics represent different phenomena.

Strong discrete sources of radio radiation are sometimes misnamed radio stars, although none of them are individual stars but should be identified with galaxies. Such sources provide an excellent grid against which the direction of the antenna can be checked. The internal consistency of the checking process shows that a few of the sources are incorrectly reported either in position or strength. Corrections will become available, but the real function of a survey is to locate the weaker, more remote sources. A catalogue of such sources in a limited portion of the sky is being prepared. Observations at radio frequencies help with the astronomical classification of the sources and bear on the theoretical problem of the formation of the universe.

By using the moon as a diffracting screen between distant radio sources and observers on the earth, Hazard (*5*) has demonstrated a powerful technique for the precise location and size estimation of radio sources that are occulted by the moon. The technique is being applied at Arecibo and results will soon be available.

Because of the great distances between the earth and even the nearby stars, signals originating in individual stars are too weak to be detected by techniques now available. If storms occur on stars, as they do on the sun, and if the radiation is enhanced markedly for brief periods, as occurs on the sun, then the enhanced radiation becomes detectable. Searches have been conducted for this type of radiation from promising stars at a number of radio astronomy observatories with some success. The sensitivity of the Arecibo facility is being brought to bear on this problem. Results are not yet available.

**References and Notes**

1. The Arecibo Ionospheric Observatory forms an integral part of the graduate program of Cornell University, and provides a unique facility for research in ionospheric physics, radar astronomy, and radio astronomy. Professors on campus and resident at the observatory guide the doctoral research of some fourteen graduate students, of whom four have conducted experiments at Arecibo. Two visiting staff members participate in the experimental program of the Observatory, and others use the facility to supplement their own research programs. Experiments are also conducted at the observatory by graduate students from other universities. The observatory is operated by Cornell University with the support of Advanced Research Projects Agency through a contract with the Air Force Office of Scientific Research.
2. W. E. Gordon, *Proc. I.R.E. Inst. Radio Engrs.* **46**, 1824 (1958).
3. K. L. Bowles, *Phys. Rev. Letters* **1**, 454 (1958).
4. ———, *Science* **139**, 389 (1963).
5. C. Hazard, *Monthly Notices Roy. Astron. Soc.* **134**, 27 (1962).
6. I thank Prof. M. H. Cohen and Dr. G. H. Pettengill for their helpful discussions during the preparation of this paper.

---

# Radiation Chemistry of the Fixation of Nitrogen

P. Harteck and S. Dondes

The fixation of nitrogen by ionizing radiation has such a tremendous potential for economic exploitation that a "breakthrough" would have a far-reaching impact on the world-wide chemical industry. A major consideration today is the possibility of using a nuclear reactor for the chemical synthesis—specifically, of using the kinetic energy of the nuclear-fission particles to produce the excited species, atoms and ions, to interact and fix nitrogen. This article presents the state of our knowledge, the unresolved problems, and some indications of possible solutions.

The term *fixation of nitrogen* denotes the chemical binding of nitrogen gas of the air to form a chemical compound. One of the simplest concepts in the fixation of nitrogen is the binding of the nitrogen gas of the air with the oxygen gas of the air. The final product is nitrogen dioxide, $NO_2$ or the dimer $N_2O_4$. Unfortunately, the intermediate reaction leading to $NO_2$ formation—namely,

$$N_2 + O_2 \rightarrow 2NO \qquad (1)$$

is endothermic by 42 kilocalories and does not proceed under normal conditions. To overcome this difficulty two major approaches have been used, one direct and the other indirect. In the direct approach, a very high temperature is used to overcome the endothermicity. This is exemplified in the Birkeland-Eyde flaming arc process and the thermal pebble bed process. Temperatures here lie in the region 2500° to 3000°C. The nitric oxide (5 to 10 percent) in thermal equilibrium at these high temperatures must be cooled immediately or it will decompose to nitrogen and oxygen. Thus a rapid chilling of the intensely hot air is required. Once the nitric oxide is cooled and in the presence of additional oxygen, the reaction

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

will produce nitrogen dioxide. The further addition of oxygen and water to the $NO_2$ will produce nitric acid, $HNO_3$.

The indirect method is best exemplified by the Haber-Bosch process, in which nitrogen and hydrogen combine at high pressures (a few hundred atmospheres) over a hot iron catalyst to produce ammonia:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (3)$$

To form nitrogen dioxide, the ammonia is burned in air or oxygen by a catalytic process to form NO. As in the direct process, the addition of oxygen and water will produce nitric acid. For the indirect process large sources of hydrogen must be readily available. Even so, the economics of the more efficient Haber-Bosch process are better than any direct process, and it is universally used.

---

Dr. Harteck is Distinguished Research Professor of Physical Chemistry at Rensselaer Polytechnic Institute, Troy, N.Y.; Dr. Dondes is a research scientist at Rensselaer Polytechnic Institute.

Table 1. Distribution of 100 electron volts absorbed in $N_2$, upon irradiation with ionizing radiation, among its primarily formed species. Number of electron volts required to form one ion pair, 34.86; $G$ (ion) = 2.86; $G$(N) = 6.0 ± 0.5.

| Species† | $E$ | $G$ | $G \times E$ | |
|---|---|---|---|---|
| 1. $N_2^+ + e^-$ | 15.5 | 2.72 | 42.1 ± 1.0 | |
| 2. $N^+ + N + e^-$ | 30.0 | 0.14 | 4.2 ± 0.2 | |
| 3. $N_2^{+*} + e^-$ | 18.5 | .03 | 0.6 ± .2 | |
| 4. $N_2{:}C^3\Pi_u$ | 11.2 | .2 | 2.2 | ± 5 |
| 5. $N_2{:}B^3\Pi_g$ | 7.4 | .3 | 2.2 | |
| 6. $N_2{:}A^3\Sigma^+_u$ | 6.2 | .4 | 2.5 | |
| 7. $N + N$ | 13 | 3.0 | 39.0 ± 5 | |
| 8. $e^-$ | 2.5 | 2.86 | 7.2 ± 3 | |
| Total | | | 100.0 ± 7.5 | |

* Excited state of $N_2^+$. † Reactions 2 and 7 have the kinetic energy of the N atom added to the dissociation energy (estimated from potential energy curves).

With the advent of large sources of nuclear energy, the direct fixation of nitrogen with oxygen is being reexamined. The high-energy radiation chemistry of the fixation of nitrogen does not involve the very high temperature which is the principal disadvantage of the flaming arc process.

## Initial Radiation Effects

When a system is irradiated with ionizing radiation the primary effects are ionization and excitation (*1*). High-energy radiations commonly used to produce these effects include alpha and recoil particles, beta rays, and x-rays or gamma rays, in addition to machine-made high-energy electrons and protons. Today, a challenge to the chemical industry is the availability of large quantities of nuclear reactor radiation consisting of a mixture of high-energy radiations. Of the nuclear reactor radiations, the kinetic energy of the fission recoil particle is about 80 percent of the total energy of fission, but the range of these particles is only about 2 centimeters in air at standard temperature and pressure and a few microns in solids. A specialized technique (one which we developed, which consists of dispersing enriched uranium oxide in glass and spinning as a fiber) (*2*) is therefore required to utilize these abundant high-energy radiations. The remaining 20 percent of the fission energy consists primarily of beta and gamma rays and high-energy neutrons, which contribute to a small extent to the primary effects of radiation, as compared with the kinetic energy of the fission recoil particles.

The energies of the high-energy radiations range from hundreds of thousands to hundreds of millions of electron volts. A molecule near or in the path of the high-energy radiations (for example, recoil particles) may absorb a small portion of that energy and be excited to various electronic levels. If the particular electronic level is below the dissociation energy, radiation may be emitted in the form of light, or the excited molecule may react with another molecule. If the electronic level is much above the dissociation energy, the excited molecule may dissociate. If the emitted radiation is resonance radiation, it may be reabsorbed in the system and, if high enough, ultimately lead to dissociation. However, if an amount of energy larger than the ionization energy is absorbed by an atom or molecule, ionization will take place in which one or more electrons are detached from the molecule, giving rise to positive ions and electrons and, by electron attachment to uncharged particles, producing negative ions. These ions may then undergo a series of reactions, such as recombination, charge transfer with surrounding molecules with lower ionization potentials, or chemical reactions with other molecules. Ion-recombination of molecules often leads to dissociation of molecules. In the irradiation of a pure substance, only recombination of the ions of this substance can occur. The presence of other substances, even in impurity concentrations, may lead to complex interactions and charge-transfer phemonena.

To interrelate the effects of the high-energy radiations of the chemical systems, a term *G value* is used, which denotes the number of molecules produced or decomposed per 100 electron volts. Since the band spectroscopy of nitrogen has been thoroughly investigated, it is possible to proportionate the 100 electron volts of energy absorbed by molecular nitrogen into excitation and ionization components. This is shown in Table 1. A similar apportionment and table could be made for oxygen. We can now examine a series of reactions leading to our desired product, nitrogen dioxide. In a mixture of nitrogen and oxygen subjected to ionizing radiation, the nitrogen and oxygen will be ionized and excited independently and proportionately to their relative stopping powers (which are about equal) and their concentrations. Immediately after the start of the irradiation and in less than $10^{-8}$ second, the following species will be formed and will be present in a stationary state: $N_2^+$, N,$N^+$, $O_2^+$, $O_2^-$, O, $O^+$, $O^-$ ($N_3^+$, and $N_4^+$) (*3*). These species may then interact among themselves, or in ion and atom reactions with $O_2$, or with products of the interactions. The predominance of one reaction over another will depend on many factors, such as temperature, pressure, mixture ratio, and radiation intensity. A knowledge of the various reactions and the effects of the enumerated variables upon them makes it possible to choose the variables in such a manner as to make the reaction yield the most favorable results.

## Reactions of Initial Radiation Products

Many ion and atom reactions can occur. Some of the more important ones are listed in Tables 2 and 3. A few examples will show the interplay of these reactions and the difficulties of assigning reactions to experimental results. Even in the collision of $N_2^+$ with $O_2$, more than one ion-molecule reaction is possible:

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+ + 3.52\ \text{ev} \qquad (4)$$

or

$$N_2^+ + O_2 \rightarrow NO^+ + NO + 4.3\ \text{ev} \qquad (5a)$$

or

$$N_2 + O_2^+ \rightarrow NO^+ + NO + 1.0\ \text{ev} \qquad (5b)$$

Since the ionization potential of oxygen is lower than that of nitrogen (15.5, compared with 12.2 ev) a charge-transfer reaction may occur, reaction 4. Since the ion-molecule reactions 5a and 5b are exothermic also, they may occur. We have observed experimentally that, under certain conditions discussed below, only the charge-transfer reaction occurs and not the ion-neutral reactions.

The basic and most important reaction, and the first step in the nitrogen fixation with oxygen, is

$$N + O_2 \rightarrow NO + O \qquad (6)$$

This reaction is exothermic and proceeds with a heat of activation of about 6 kilocalories. The NO thus formed will react in two different ways:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

and

$$N + NO \rightarrow N_2 + O \qquad (7)$$

Reaction 2 is the desired reaction. Reaction 7 is very fast (the reaction rate is $3 \times 10^{-13}$ cm$^3$ per particle per second),

Table 2. Atom reactions most important to the nitrogen fixation process. In the dissociation of $N_2$ (reaction 1), the N atoms formed may not be thermalized but have kinetic energy and may react with $O_2$ at lower temperatures faster than indicated by reaction 3.

| | Reaction | Item |
|---|---|---|
| 1. | $N_2 \rightarrow 2N$ | $\Sigma G_{N2} \cong 5.5$ |
| 2. | $O_2 \rightarrow 2O$ | $\Sigma G_{O2} \cong 8$ |
| 3. | $N + O_2 = NO + O$ | $k_3 = 10^{-16\pm0.2}$ cm$^3$ sec$^{-1}$ |
| 4. | $NO_2 + O = NO + O_2$ | $k_4 = 10^{-12}$ cm$^3$ sec$^{-1}$ |
| 5. | $2NO + O_2 = 2NO_2$ | $k_5 = 10^{-37\pm.02}$ cm$^3$ sec$^{-1}$ |
| 6. | $2NO_2 \rightleftarrows N_2O_4$ | |
| 7a. | $NO_2 \rightarrow NO + O$ | $-G_{NO_2} = 12$ |
| 7b. | $NO_2 \rightarrow N + O + O$ | $-G_{NO2} = 0.5$ |
| 8a. | $N + NO_2 = 2NO$ | $k_{8a} = 5 \times 10^{-13\pm0.5}$ cm$^3$ sec$^{-1}$ |
| 8b. | $N + NO_2 = N_2O + O$ | $k_{8b} = 3.2 \times 10^{-13\pm0.5}$ cm$^3$ sec$^{-1}$ |
| 8c. | $N + NO_2 = N_2 + 2O$ | $k_{8c} = 2 \times 10^{-13\pm0.5}$ cm$^3$ sec$^{-1}$ |
| 8d. | $N_2O_4 + N \rightarrow NO_2 + 2NO$ | |
| 9. | $NO + N = N_2 + O$ | $k_9 = 10^{-12\pm0.5}$ cm$^3$ sec$^{-1}$ |
| 10a. | $N_2O \rightarrow N_2 + O$ | $\left.\begin{array}{l}-G_{N_2O} = 9\\ -G_{N_2O} = 3\end{array}\right\} = 12$ |
| 10b. | $N_2O \rightarrow NO + N$ | |
| 11. | $NO \rightarrow N + O$ | $-G_{NO} = 3.5$ |
| 12a. | $NO^+ + e^- = N + O$ | |
| 12b. | $NO^+ + e^- = NO + h\nu$ | |
| 12c. | $NO + M^+ = NO^+ + M^*$ | |

* Precise relative to one another.

so that in practice a very low steady-state concentration of NO is required to reduce its effect. The $NO_2$ formed in reaction 2 may react in three different ways:

$$NO_2 + N \rightarrow 2NO \tag{8}$$

$$NO_2 + N \rightarrow N_2O + O \tag{9}$$

$$NO_2 + N \rightarrow N_2 + 2O \tag{10}$$

Of these three, only reaction 8 is favorable. Note that reactions 8, 9, and 10, and 7 consume the nitrogen atoms needed in the initial reaction 6. If the gas mixture of nitrogen and oxygen is irradiated longer than $10^{-3}$ second, not only are $N_2$, $N_2^+$, $N^+$, $O_2$, $O_2^+$, $O_2^-$, O, $O^+$, and $O^-$ present but also NO, $NO^+$, $NO_2$, $NO_2^+$, $NO_2^-$, $N_2O^+$, $O_3$, $NO_3$, and $N_2O_5$, and possibly other species unknown at present. To a degree depending upon concentrations, the behavior of this mixture, when it is subjected to additional irradiation, will differ from that of the original mixture of nitrogen and oxygen. Therefore, yields or *G* values for the $NO_2$ and $N_2O$ formation are comparable only if the overall mechanism is known.

Other reactions of Tables 2 and 3 can be discussed similarly, but such discussion is beyond the scope of this article.

## Experimental Evidence

The irradiation of capsules containing mixtures of nitrogen and oxygen has provided the basic evidence for the fixation of nitrogen (*4*). The products of the irradiation have been $NO_2$ and $N_2O$, with maximum *G* values of 7.2 and 3, respectively. Of the variables enumerated above, high pressures (above 10 atmospheres), temperature in the region of 200°C, and a mixture ratio approaching that of air are most favorable for high yields. To determine how the reaction proceeds, capsule experiments have been carried out under various conditions between limits imposed by the available facilities. Thus we have irradiated the capsules for thousands of hours, to determine whether kinetic radiation equilibrium (the state where further irradiation does not change the ratio of products and reactants) can be achieved. Similarly, we have conducted irradiation experiments to determine whether all the oxygen has been consumed in nitrogen-oxygen mixtures. Under certain conditions this has been achieved (Fig. 1). The rate for the decomposition of the products and the mechanisms of their decomposition have also been studied (*5*), the *G* values for the decomposition of the oxides of nitrogen—$N_2O$, NO, and $NO_2$—being 12, 3.5, and 0.5, respectively. In none of the capsule experiments conducted to date have chain reactions been observed. Amechanism with $G_{NO_2}$ above 10 would make the process economically competitive with existing processes. From our results it appears that this yield can only occur if all the N atoms which come from ion recombination and excitation react only according to reaction 6. Other reactions producing additional fixed nitrogen in appreciable quantities are not known at this time.

With experimental information that nitrogen can be fixed through ionizing radiation, but with a yield limited to a *G* value of about 6, attention has been drawn to other techniques in an effort to increase the yields, or to determine why the yields converge at a value of 6. One method under study in our laboratories is a labeling technique. Since the basic reaction is reaction 6, the number of nitrogen atoms produced in the irradiation process must be known. By capsule irradiation of a mixture of $^{14}N_2$ and $^{15}N_2$ (mass units 28 and 30), the number of nitrogen atoms produced can be determined from the resulting concentration of $^{14}N^{15}N$ (mass unit 29). If ion recombination and excitation both produced nitrogen atoms, we see, from Table 1, that 11.7 nitrogen atoms should be formed per 100 electron volts (*6*). Experiments with a mixture of pure $^{14}N_2$ and $^{15}N_2$ (oxygen concentration less than 1/10,000) gave a result of 11.5, in excellent agreement with the prediction. The introduction of about 1 percent oxygen reduced this $G_N$ value to about 6, showing the predominance of reaction 4 over reactions

Table 3. Ion molecule reactions (*12*). These reactions should be used with caution when applied to radiation chemistry using a nuclear reactor.

| | Reaction | $k$ (cm$^3$ sec$^{-1}$) |
|---|---|---|
| 1. | $N_2^+ + O_2 \rightarrow N_2 + O_2^+$ | $k_1 > k_2$ or $k_3$ |
| 2. | $N_2^+ + O_2 \rightarrow NO^+ + NO$ | $k_2 \leq 2.1 \times 10^{-13}$ |
| 3. | $N_2 + O_2^+ \rightarrow NO^+ + NO$ | $k_3 \leq 2.1 \times 10^{-13}$ |
| 4. | $O^+ + N_2 \rightarrow NO^+ + N$ | $k_4 \sim 2.2 \times 10^{-11}$ |
| 5. | $N^+ + O_2 \rightarrow NO^+ + O$ | $k_5 \sim 1 \times 10^{-10}$ |
| 6. | $N_2^+ + N_2O \rightarrow NO^+ + N_2 + N$ | $k_6 \sim 4 \times 10^{-10}$ |
| 7. | $N^+ + N_2O \rightarrow NO^+ + N_2$ | $k_7 \sim 5.5 \times 10^{-10}$ |
| 8. | $O^+ + N_2O \rightarrow N_2O^+ + O$ | $k_8 \sim 5.5 \times 10^{-10}$ |
| 9. | $O_2^+ + N_2O \rightarrow NO^+ + NO_2$ | $k_9$, not known |
| 10. | $N_2^+ + NO \rightarrow N_2 + NO^+$ | $k_{10}$, not known |
| 11. | $N_2^+ + NO_2 \rightarrow NO^+ + N_2O$<br>or $NO^+ + N_2 + O$<br>or $NO^+ + NO + N$ | $k_{11}$, not known |

*5a* and *5b*. Further increase in the oxygen concentration reduced the $G_N$ value of nitrogen atoms below 6. The overall process is evidently complex. Using this technique, Anbar and Perlstein (*7*) have recently determined the $G_N$ values independently and found them to be in quite satisfactory agreement.

In Table 1 a small fraction of the energy absorbed by the nitrogen molecule is shown as emitted light. This fraction was determined from experimental irradiation of pure nitrogen with polonium-210 alpha particles, in the course of which light was emitted (*8*). The spectroscopic analysis of this light showed which electronic levels of the nitrogen molecules were primarily excited and, from the intensity of the band spectra, the relative abundance of the species. These abundances were related to the overall excitation and ionization processes. However, these experiments show that, although energy is absorbed by a nitrogen molecule, not all of it is available for the dissociation of nitrogen and subsequent chemical synthesis; some of it is lost by light emission.

To reduce the negative effects of reactions 7, 9, and 10, the NO and $NO_2$ should be removed as quickly as possible. One method is to neutralize these acidic oxides of nitrogen with a base to form a salt that does not decompose readily. We conducted experiments on the irradiation of air in which the walls of the capsule containing the air were coated with solid KOH. In control experiments, noncoated capsules containing air were irradiated under identical conditions. The results were as anticipated. In the coated vessels practically all the oxygen was consumed and no $N_2O$ was observed. In the noncoated vessel, a substantial quantity of oxygen remained, together with a similar amount of $N_2O$. These experiments confirmed the belief that in the coated vessels there was no steady-state concentration of NO and $NO_2$ for the nitrogen atoms to react with, by way of reactions 7 and 9. Also, in the coated vessels the NO and $NO_2$ appeared as $KNO_2$ and $KNO_3$.

The complexity of the reactions in the irradiation of nitrogen-oxygen systems is demonstrated by an experiment in which air at a pressure of 1 atmosphere is irradiated with polonium-210 alpha particles in a static system, and the products of the irradiation are continuously analyzed with an infrared spectrophotometer. Our results showed that the initial products were $N_2O$, $O_3$, and $N_2O_5$. As the duration of the irradiation increased, a point was reached where the ozone concentration was diminished and finally disappeared. At this point the $N_2O_5$ decomposed and $NO_2$ began to be observed. Further irradiation only produced additional $N_2O$ and $NO_2$. The explanation of this phenomena has been reported elsewhere (*9*).

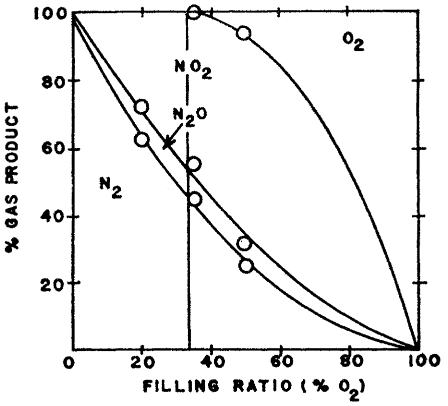

Fig. 1. Kinetic radiation equilibrium diagram for $N_2$–$O_2$ system at high pressure and 85°C. A vertical line at the proper filling ratio will be divided into segments that are proportional to the partial pressures of the four gaseous components of the mixture. The sample line shows the situation for 33 percent $O_2$.

The experimentation described has been conducted in capsules and other static systems. In the past few years Rensselaer Polytechnic Institute has operated a loop at the Brookhaven National Laboratory; the latest modification of the operation consists in cycling nitrogen-oxygen-helium mixtures at pressures of 68 atmospheres over glass fibers (located within the nuclear reactor) containing 1.5 grams of enriched uranium. (The purpose of the helium is to increase the heat conductivity of the gas mixture and prevent the glass fibers from melting). The results showed that $N_2O$ and $NO_2$ were formed, with $G_{N_2O}$ of 1 and $G_{NO_2}$ of 0.5. Since this ratio of $G_{NO_2}$ to $G_{N_2O}$ is much less than the ratio in the capsule experiments, a substantial amount of $G_{NO_2}$ must have been consumed. Lowering the pressure decreased the yields. Although the yields were poor (for reasons indicated below), the loop experiment showed the contaminants of the gas to be iodine-131, xenon-131, and xenon-135. The iodine-131 is trapped in a silver nitrate trap in series with the gas flow. Through numerous tests the only radioactive product observed was xenon, which is readily distilled from nitrogen dioxide. This finding is important if the fixed nitrogen is to be consumed in any way by humans. In laboratory techniques the concentration of the xenon is taken as an indication of the energy absorbed by the gas system. This loop at Brookhaven may be considered a semi-pilot plant and a reactor within a reactor, and a forerunner in the utilization of nuclear reactors for the chemical synthesis of fixed nitrogen.

## Problem Areas

Since the radiation chemistry of the nitrogen fixation with oxygen is so complex, a number of problems remain to be solved. A major area is the disagreement of investigators concerning the maximum $G_{NO_2}$ values obtainable in the fixation of nitrogen with oxygen. One cause of this disagreement is the attempt by some to interrelate the results of experiments in which $NO_2$ and $N_2O$ are produced in amounts of less than 1 percent and the results of other experiments in which the figure is over 5 percent. Comparison is only possible through extrapolation to the reaction rates at the very beginning of the irradiation, since the concentration of the products plays a major role in the overall kinetics of the system.

Another difficulty is that of container material. Some investigators have used stainless steel vessels, others quartz vessels. Those using stainless steel vessels have obtained $G_{NO_2}$ values of 6 and 7.2, whereas those using quartz vessels have obtained values of less than 6, many results being substantially below that figure. Although the use of quartz is convenient in experiments conducted within a nuclear reactor, the fluorescence of the quartz in the far-ultraviolet may be one of the major problems. Recently it has been found at Rensselaer that $NO_2$ and NO are decomposed by ultraviolet light of 2062 angstroms (equivalent to energy of about 6 ev). Quartz irradiated with ionizing radiation will emit strong ultraviolet irradiation in this wavelength region. Therefore photolysis by the fluorescing quartz supplements the destruction of fixed nitrogen by the ionizing radiation, resulting in lower overall yields. Since the variable impurities within commercial quartz may augment or decrease the intensity of the fluorescence, the experimental results will vary. The effect of photolysis may also be a major problem in the use of glass fibers containing enriched uranium in our loop experiment. Therefore a new in-pile section containing no glass fibers is being constructed to parallel the section containing glass fibers which is now being used. A comparison of the results will determine the extent of the photolytic effect.

As shown previously, the irradiation of pure nitrogen causes excitation, followed to a small extent by light emission. The total energy absorbed is therefore not available for chemical synthesis. To determine the extent of this light emission an experiment is being designed in which the kinetic energy of the fission fragments is used as the source for exciting and ionizing gaseous nitrogen within the nuclear reactor, and the light emitted is conducted through a quartz light pipe to an emission spectrograph for observation of the emission spectra. Since glass fibers containing enriched uranium will be used for this experiment, the effects of the fluorescence of the silica will also be examined.

In the experiments with $^{14}N_2$ and $^{15}N_2$, it was shown that oxygen quenches the production of the nitrogen atoms. This is indeed a difficult problem to solve. One suggestion is to use extremely high pressures—for example, 1000 atmospheres—where the oxygen concentration would be 0.1 to 0.3 percent. The irradiation of this mixture at this very high pressure would permit formation of nitrogen dioxide; however, the oxygen concentration would be so low as not to quench nitrogen atom formation by charge transfer (reaction 4). Unfortunately, facilities to conduct such an experiment are not readily available.

A suggested method that might increase the yield of fixed nitrogen is that of removing the NO and $NO_2$ as formed. Capsule experiments have shown this to be possible. The use of KOH is not feasible in a dynamic loop experiment. However, in capsule experiments water vapor at low partial pressures has been observed to reduce the $NO_2$ concentration, forming $HNO_3$ without taking part in the reaction. This may be a fruitful approach, since $HNO_3$ can be readily condensed out of the circulating gas steam.

Unfortunately, no radiation research reactor facility is available for conducting specialized capsule and loop experiments. Existing facilities at nuclear reactor sites were not designed for the many variations in experimental conditions required in radiation chemistry. Facilities for irradiation at extremes of temperature and pressure, to determine mechanisms and direct reactions, require substitutive techniques which are inadequate for the radiation chemist. Availability of a nuclear reactor designed for radiation research may overcome these problems.

The radiation chemistry of fixed nitrogen shows that the nitrogen may be fixed with atmospheric oxygen to yield nitrogen dioxide. Technical feasibility studies have been made by Brookhaven nuclear engineers using cores of fissionable material in the form of fibers, ribbons, or powder (*10*). Chemonuclear plants have been designed to produce nitrogen dioxide in quantities of 180 to 900 metric tons per day. Dual-purpose reactors have been designed for producing fixed nitrogen and electrical power as well. Economic feasibility studies based on various reactor designs show that $NO_2$ could be produced by chemonuclear reactors at a cost not very much higher than that of existing processes. With the population explosion and associated agricultural needs, the requirements for fixed nitrogen will continue to increase. Thus, the production of $NO_2$ from a single nuclear reactor would not saturate the market in the way that reactor production of other products—for example, ethylene glycol (antifreeze) from methanol—would. The second-generation loop being designed by Brookhaven National Laboratory and the basic research being conducted around the world testify to the intensity of investigation in this field.

Despite the myriad problems and the extensive experimentation and development that are required to make chemonuclear-reactor production of fixed nitrogen in the form of $NO_2$ an economical commercial process, we are optimistic. There are two possible avenues to a breakthrough. One is steady systematic research on the nitrogen fixation process, and steady development to achieve higher yields and lower costs, so that, relative to the rising prices of natural gas, a break-even point can be reached; the other is some "lucky" innovation by means of which $G_{NO_2}$ equal to 10 or more may be achieved.

## Other Nitrogen Fixation Processes

There are two other systems for fixing nitrogen: the nitrogen-hydrogen system for producing ammonia and the nitrogen-sulfur system for producing $N_4S_4$. We have not pursued these extensively as they seem much less promising than the nitrogen-oxygen system. The irradiation of a nitrogen-hydrogen mixture produces ammonia with a $G_{NH_3}$ of about 0.7. Even if this value could be raised to 7, the high cost of hydrogen and the lower $G$ value for ammonia relative to fixed nitrogen in its oxidized form would still make the process unattractive economically.

When the sulfur compound $N_4S_4$ has been produced through irradiation of nitrogen and sulfur vapor mixtures in a nuclear reactor at 300° to 400°C, the yield has been poor. This poor yield results from the decomposition of $N_4S_4$ at temperatures above 200°C. However, temperatures above 300°C are required to vaporize the sulfur sufficiently to produce the proper partial pressure in the nitrogen-sulfur mixture. Earlier experiments in which nitrogen atoms produced in a glow discharge reacted very quickly with sulfur vapor led us to undertake irradiation experiments with a certain degree of optimism.

## Hydrazine from Ammonia

Although not a nitrogen fixation process as previously defined, the irradiation of ammonia in the liquid or gas phase, conducted by other investigators (*11*) to produce hydrazine, should be mentioned. The overall equation for the hydrazine formation is:

$$2NH_3 \rightarrow + N_2H_4 + H_2 \qquad (11)$$

Despite the apparent simplicity of reaction 11, the kinetics of the system are as complex as others involving nitrogen. Also, less is known about the chemistry of the ions and radicals involved in this system. Upon irradiation of ammonia, $NH_2$, NH, $H_2$, N, and $NH_3^+$ will be produced. The $NH_3^+$ will react quickly with an $NH_3$ molecule:

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \qquad (12)$$

Although many of the chemical species will interact among themselves, only reaction

$$NH_2 + NH_2 \rightarrow N_2H_4 \qquad (13)$$

is known to produce $N_2H_4$, although the reaction

$$NH + NH_3 \rightarrow N_2H_4 \qquad (14)$$

should not be discarded. From experiments in which liquid ammonia was irradiated with gamma rays, $G_{N_2H_4}$ was found to be about 0.1, and the radiation equilibrium was found to occur at an $N_2H_4$ concentration of about $10^{-4}$. However, similar experiments with liquid ammonia but with fission recoil particles gave $G_{N_2H_4}$ values of 1.2 to 2. The work (*11*) with fission particles has proceeded to the loop-operation stage, which involves the use of enriched uranium oxide in liquid ammonia as a slurry. Results of the work at this stage have not been officially reported. Chemonuclear designs have indicated that the process would be economically practical if a hydrazine concentration of a few percent with a $G_{N_2H_4}$ of about 1.5 could be obtained.

Finally, a cursory glance should be given to a few present uses of ionizing radiation in industry and a few novel concepts concerning radiation chemistry that are in early stages of investigation. The industrial processes include irradiation of polyethylene coating on wires and irradiation of ethylene and hydrogen bromide with gamma rays to form ethylbromide, by the Dow Chemical Company. The novel concepts under investigation concern the production of ozone in liquid oxygen and the formation of carbon suboxide in the irradiation of CO. Ozone is a cheap oxidant, and carbon suboxide is a starting material in the manufacture of some organic chemicals or pharmaceuticals.

Although no "demonstration" nuclear plants for nitrogen fixation exist at present, the radiation chemistry of the fixation of nitrogen points to the probability that nuclear energy will eventually be directly used for chemical synthesis.

### References and Notes

1. For a review, see the classic work of S. C. Lind, *Radiation Chemistry of Gases* (Rheinhold, New York, 1961).
2. P. Harteck, S. Dondes, P. Lockwood, "Glass Fibers Containing Fissionable and Fertile Materials," *AEC Document NYO-9968* (1961).
3. At this time evidence of $N_3^+$ and $N_4^+$ occurring in a mixture with a substantial concentration of $O_2$ has not been verified.
4. P. Harteck and S. Dondes, *Z. Elektrochem.* **64**, 983 (1960); ———, *J. Phys. Chem.* **63**, 956 (1959); M. Steinberg, "Chemonuclear Reactors and Chemical Processing," *Advances in Nuclear Science and Technology*, E. J. Henley and N. Kouts, Eds. (Academic Press, New York, 1962), vol. 1, p. 247.
5. P. Harteck and S. Dondes, *Nucleonics* **14**, No. 3, 66 (1956); *J. Chem. Phys.* **27**, 546 (1957).
6. From Table 1 we see that, since 2.86 ion pairs are formed per 100 electron volts, then 5.72 N atoms should be formed as a result of ion-electron recombination. In addition, six atoms should be formed by excitation and dissociation of three nitrogen molecules. This totals 11.7.
7. M. Anbar and P. Perlstein, *J. Phys. Chem.* **68**, 1234 (1964).
8. S. Dondes, P. Harteck, C. Kunz, *Z. Naturforschung* **19a**, 6 (1964).
9. P. Harteck and S. Dondes, *J. Chem. Phys.* **28**, 975 (1958).
10. G. Lellouche and M. Steinberg, "Industrial Chemical Production by Chemonuclear Processes with Special Reference to the Production of Fixed Nitrogen," *AEC Rept. BNL-574* (1959).
11. *Aerojet General Nucleonics Repts., ASD Interim Repts. 7-840A* (*I* to *XI*) (July 1961 to Oct. 1963).
12. A. Galli, A. Giardini-Guidoni, G. G. Volpi, *J. Chem. Phys.* **39**, 518 (1963); G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, G. G. Volpi, *ibid.* **40**, 3450 (1964).

---

# Academic Organization in Physical Science

## Universities should organize a unified approach to all pure and applied physical science.

Henry G. Booker

What constitutes the physical science area of a university? Of what should it consist in the future? How should the various facets fit together? Where does a subject like geophysics fit into the overall operation? What kind of academic structure should house all these activities?

By the physical science area of a university I mean all those activities on the campus for which physics is the basis. Besides the physics department, the physical science area includes departments such as geophysics, earth sciences, meteorology, and astronomy. It also includes those areas of the campus where students who ultimately hope to follow the profession of engineering are engaged in study and research in physical science. These are departments with such names as aerospace engineering and electrical engineering. However, I would not include in the physical science area of a university any engineering department that still regarded its prime function as the professional training of students in empirical design; frankly, I would not include such an engineering department in a university at all! By the physical science area of a university I mean, therefore, the departments dealing with theoretical physics, experimental physics, observational physics, and applied physics; with present university organization this area includes the dynamic part of the Engineering College.

An awkward feature of the physical science area of a typical American university is that it is illogically bisected by a major administrative division of the university. Part of the physical science area is usually located in the college of humanities and sciences, while part is located in the college of engineering. In an Ivy League university with which I am familiar, plasma physics is studied in its laboratory form in the department of aerospace engineering, in its upper-atmospheric form in the department of electrical engineering, in its cosmic form in the department of astronomy, and in its solid-state form in the department of physics. Of these four departments, two are responsible to the dean of engineering and two to the dean of arts and sciences. Thus, the coordination of even one facet of physics involves not only four department heads but two deans, not counting the dean of the graduate school. And yet it only takes one dean, the dean of arts and sciences, to handle such diverse subjects as quantum theory and Greek literature. Universities are well organized to do many things that do not need doing, but in physical science they are often poorly organized

The author is IBM Professor of Engineering and Applied Mathematics and a member of the staff of the Center for Radiophysics and Space Research, Cornell University, Ithaca, N.Y.