is there reason to believe that radiation levels have changed appreciably during the quarter-billion years or so of existence of the higher plants. Rather, it seems that we must look further for other environmental factors or combinations of factors that have affected the evolution of that constellation of characteristics we measure when we measure radiosensitivity, including especially chromosome size.

It is an intriguing if somewhat oversimplified hypothesis that sensitivity to radiation damage is a measure of sensitivity to environmentally induced mutation (mutation is used in its broadest sense). It seems reasonable to accept the concept that rates of mutation tend toward some optimum, which is under hereditary control (*24*). If the rate were too high, there would be reduction in reproductive success; if too low, there would be insufficient variability to meet the evolutionary demands of constantly changing environments.

Certainly it is conceivable that environments vary in capacity to produce mutations. If, on the basis of current evidence about mutations, one were to seek a mutagenic natural environment (independent of radiation intensity), he would probably seek one characterized by extremes: extremes of temperature, moisture availability, and solar radiation. One thinks immediately of surfaces exposed to the sun: soil, rock, bark. The evidence that I report suggests strongly that plants that normally inhabit such surfaces—algae, lichens, mosses, and prostrate-growing vascular plants—are more resistant to ionizing radiation (and doubtless to many other stresses) than plants of more ameliorated environments such as forests.

Whether this suggestion will prove to be true when examined in a larger context than has yet been possible remains to be seen. Nonetheless, we now infer that ability to survive such rigorous environmental conditions also confers in some degree, at least, resistance to ionizing radiation. The factors that confer resistance involve growth form, length of life cycle, regenerative capacity, and cytological characteristics, especially average interphase chromosome volume. Experimental examination of this question is a current challenge to radiation research. Only by willingness to look at such really tough questions will we gain further insight into both radiation and the patterns of nature.

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Atom Reactions in Flow Tubes

Reactions of atoms and free radicals from electric discharges can be studied in fast flow systems.

B. A. Thrush

Free atoms, such as oxygen and hydrogen, and free radicals (for example, OH) play vital roles in combustion reactions, in the chemistry of the upper atmosphere, and in radiation chemistry. With these systems, it is difficult to isolate an elementary step, but reliable experimental data on such steps are important in the development of theoretical chemical kinetics, as well as for establishing overall reaction mechanisms. The production of free atoms and radicals in electric discharges has been known for many years, but the sudden growth in the use of this method in the last decade has been greatly stimulated by the development of specific methods for determining concentrations of atoms or free radicals.

The long-lived yellow afterglow of "active nitrogen" produced by a discharge through nitrogen gas was discovered nearly a hundred years ago. Over the period 1910–1940, Strutt (Lord Rayleigh) (*1*) showed that this afterglow was associated with the recombination of ground-state nitrogen atoms formed in the discharge. The use of this afterglow, or of related afterglows, to measure the concentrations of free atoms came later, when a variety of experimental techniques showed that the main reactive products of electric discharges through gases at low pressures were free atoms in their electronic ground states. The

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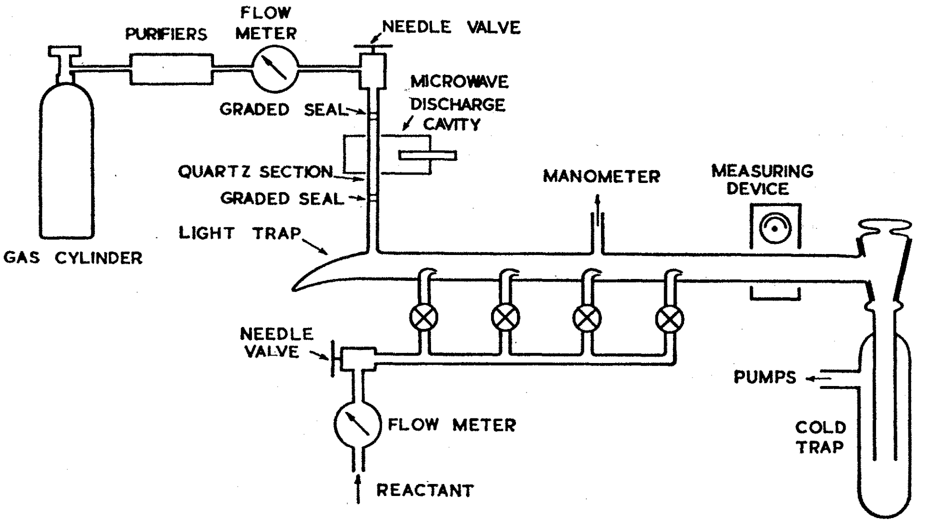

Fig. 1. Typical apparatus for discharge-flow experiments.

use of a pump to withdraw products from a steady discharge so that their reactions could be studied in a flow tube came in the 1920's with the work of Wood (*2*), and of Bonhoeffer (*3*) on hydrogen atoms.

Figure 1 illustrates the layout of a typical discharge-flow apparatus. Metered flows of carefully purified gases from cylinders pass through an electrodeless discharge into the reaction tube. The light trap prevents radiation from the discharge photolyzing the reactants or interfering with optical measurements. At total pressures typically between 0.5 millimeter and 5.0 millimeters of mercury, a radio-frequency or microwave discharge of 100 watts gives on the order of 1-percent dissociation into free atoms. Consistently pure gases must be used, as trace impurities are often almost completely dissociated in the discharge, giving reactive species (for example, hydrogen atoms, from water). There is some temptation to add controlled amounts of certain impurities, such as oxygen to nitrogen, since oxygen is an efficient catalyst of the main dissociation process and greatly increases the yield of nitrogen atoms.

In the absence of added reactant, free atoms decay by two recombination processes: recombination on the walls and in the gas phase. The latter process requires the collision of two atoms in the presence of a third body for stabilization; under typical conditions (1 percent atoms; total pressure, 2 millimeters of mercury) this gives a half-life on the order of 1 second for free atoms. The fraction of wall collisions, by atoms, which result in recombination (γ) depends on the nature of the surface. Nitrogen or oxygen atoms on glass or quartz surfaces commonly give $\gamma \sim 10^{-5}$, but acid or Teflon coatings are needed to obtain such low values of γ for hydrogen, chlorine, or bromine atoms. With a flow tube about 2 centimeters in diameter and $\gamma = 10^{-5}$, the half-life for free atoms that decay by wall recombination is also about 1 second (*4*), and there is a negligible radial concentration gradient in the flow tube associated with the diffusion of atoms to the walls (*4*).

If the flow velocity of the gas is known, measurement of the decay of atoms down the flow tubes gives the kinetics of atom decay. The addition of a reactant at one of the mixing jets accelerates this decay, and the rate constant for the reaction of the reactant with the atom concerned can be determined from this acceleration. Generally it is simplest to use a fixed observation point and to vary the reaction time by adding the reactant at different points upstream; this method automatically allows for the parallel decay processes mentioned above (*5*). Mixing of the added reactant is rapid, since gaseous diffusion coefficients are of the order of 200 square centimeters per second at pressure of 1 millimeter of mercury. Linear flow velocities are normally 100 to 500 centimeters per second; at lower velocities diffusion of reactants along the flow tube can cause errors, while, at higher velocities, pressure drop in the system can become significant (*4*).

Measurement of Absolute Concentrations

In the early investigations, only nonspecific methods for determining atomic concentrations were available (*6*). These included measurement of the heat released by the recombination of atoms on a metal surface or of the pressure change on recombination. One ingenious method is measurement by means of the Wrede gauge; this involves measuring the steady-state pressure difference established across a small orifice when atoms and molecules flow through the orifice onto a catalyst for recombination but only molecules return.

The specific methods for measuring the concentrations of atoms and free radicals all involve forms of spectroscopy. With mass spectrometry there is a difficulty—the considerable extent to which these species recombine on metal surfaces near the ion source of normal instruments. This difficulty can be largely overcome with a molecular-beam inlet system in which the beam is chopped to discriminate against particles which have suffered wall collisions (*7*). Mass spectrometry can also give limited information about excited atoms or molecules which have lower ionization potentials than the ground-state species. Like mass spectrometry, electron spin resonance involves elaborate and complex instrumentation. It provides a very sensitive method of detecting paramagnetic species in gases —that is, free atoms, certain diatomic radicals, and some metastable excited molecules such as $O_2(^1\Delta_g)$.

Some diatomic species do not have resonances at accessible field strengths, and the spectra of nonlinear molecules in the gas phase so far have proved too complex to analyze. Calibration requires considerable care to avoid errors, particularly those due to saturation of the absorption lines by the microwave power used to measure them (*8*).

Electronic absorption spectroscopy is more suitable for free radicals than for atoms, since the resonance lines of hydrogen, nitrogen, oxygen, and the halogens all lie in the vacuum ultraviolet; these have been observed in discharge-flow experiments, but accurate measurements are difficult (*9*). A discharge through water vapor has been used as a source of OH radiation for measuring the concentration of this important species in discharge-flow experiments (*10*). Figure 2 shows a double-beam photometer system, used in our laboratory, in which CN violet emission is used as a source in measuring

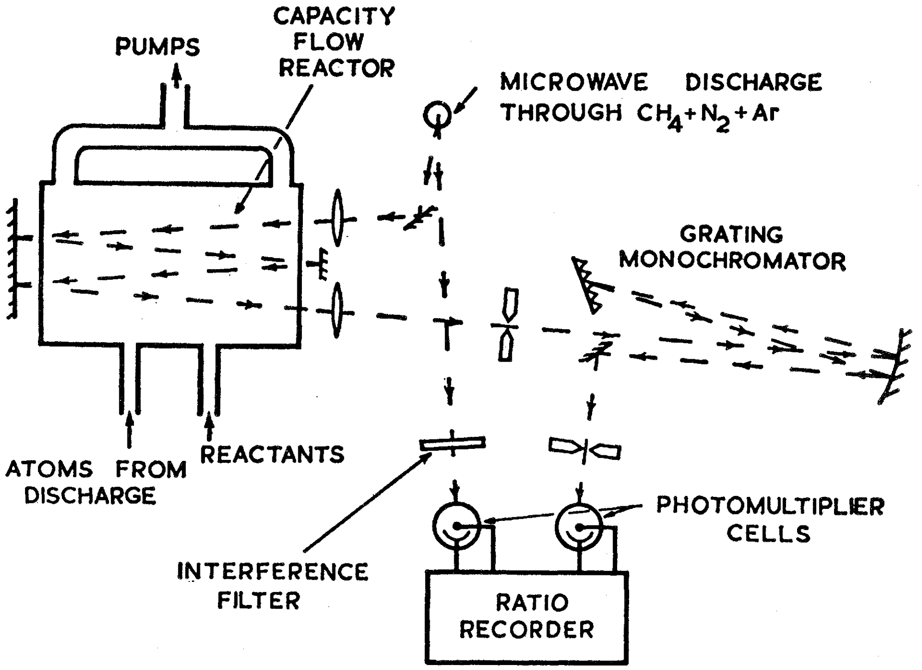

Fig. 2. Capacity flow reactor with double-beam photometer for measuring CN-radical concentration by absorption spectroscopy.

partial pressures of the CN radical as low as 10^{-6} millimeter of mercury. This apparatus has a capacity flow reactor, where reaction occurs uniformly throughout a comparatively large vessel into which free atoms and other reactants are steadily introduced and from which the products are pumped. These systems are suitable for measuring species having longer reaction times, since they give smaller contribution from surface effects than linear flow systems do.

The chemiluminescent recombination reactions of free atoms provide the most convenient and popular method of measuring atomic concentration. This is well illustrated by the titration of the nitrogen atoms in active nitrogen oxide (*11*) according to the rapid stoichiometric reaction

$$N + NO = N_2 + O + 75 \text{ kcal/mole} \quad (1)$$

Figure 3 shows how the intensities of the various chemiluminescent emissions change as increasing flows of nitric oxide are added to active nitrogen. The yellow nitrogen afterglow, the intensity of which is proportional to the square of the nitrogen atom concentration, is replaced by the blue nitric oxide afterglow which accompanies the reaction

$$N + O + M = NO + M.$$

Both these glows are extinguished when the flow of added nitric oxide exactly balances that of nitrogen atoms, the gas downstream appearing dark because oxygen atom recombination gives no visible emission. Addition of excess nitric oxide gives the yellow-green "air afterglow" associated with the combination of oxygen and NO to give electronically excited NO_2 molecules.

Similarly, oxygen atoms can be titrated with nitrogen dioxide (*12*) according to the reaction

$$O + NO_2 = NO + O_2 + 46 \text{ kcal/mole.} \quad (2)$$

This is significantly slower than reaction 1, but nevertheless it occurs at one collision in 100 between oxygen and NO_2. In this case the air afterglow produced by the nitric oxide generated in reaction 2 provides the "indicator," its extinction corresponding to the complete consumption of oxygen atoms.

The intensities of these afterglows are usually measured with a photomultiplier cell fitted with the appropriate light filters. Such a system combines high sensitivity with excellent linearity over a wide range, and once it has been calibrated for absolute atom concentrations, through use of one of the titrations indicated above, or perhaps by means of a calorimeter, it can be used over a wide range of concentrations. For oxygen atoms, known flows of nitric oxide would be added upstream of the photomultiplier, and the intensity of the air afterglow, which is proportional to $[O] \cdot [NO]$, would be measured. A similar technique can be used to find hydrogen atom concentrations, where the red and infrared emission by electronically excited HNO is proportional (*13*) to $[H] \cdot [NO]$. Recombination of chlorine atoms and of bromine atoms also gives glows whose intensities are proportional to $[Cl]^2$ and to $[Br]^2$, respectively (*14*).

It should be noted that these glows are not due to the formation of excited molecules in a simple two-body association. The excited molecules are normally found in a three-body process, and are removed both by radiation and by collisional quenching; for example,

$$H + NO + M = HNO^* + M \quad (3)$$
$$HNO^* = HNO + h\nu \quad (4)$$
$$HNO^* + M = HNO + M \quad (5)$$

For this reason the observed intensities of the afterglows may depend on the pressure and nature of the carrier gas used.

Application to Hydrogen-Oxygen Systems

The use of discharge-flow systems to determine the rate constants for elementary steps in the hydrogen-oxygen reaction illustrates the technique well. Hydrogen and oxygen undergo a chain reaction which is explosive between two well-defined pressure limits at temperatures in the range 350° to 500°C (*15*). (Here I ignore its behavior at very high pressures.) The mechanism of the reaction is thought to be

$$H + O_2 = OH + O - 17 \text{ kcal/mole} \quad (6)$$
$$O + H_2 = OH + H - 2 \text{ kcal/mole} \quad (7)$$
$$OH + H_2 = H_2O + H + 15 \text{ kcal/mole (twice),} \quad (8)$$

giving $H + 3H_2 + O_2 = 2H_2O + 3H$.

The reaction generates more hydrogen atoms than it consumes and is therefore autocatalytic and explosive unless hydrogen atoms are rapidly removed. This removal occurs by diffusion to the walls at low pressures (the first explosion limit) or by the recombination reaction

$$H + O_2 + M = HO_2 + M + 47 \text{ kcal/mole} \quad (9)$$

at high pressures (the second explosion limit).

Detailed studies of the reaction have yielded rate constants for reactions 6 and 9 and for *either* reaction 7 or 8,

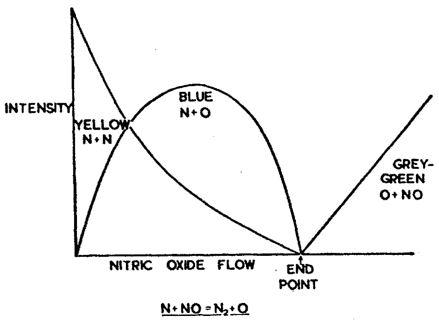

Fig. 3. Behavior of the afterglows in the titration of atomic nitrogen with nitric oxide, according to the reaction $N + NO = N_2 + O$.

but these rate constants are based on the calculated loss of hydrogen atoms by wall diffusion and on the assumed reaction mechanism.

Reaction 7 can be investigated relatively easily (*5*), although the experiments must be made in the absence of molecular oxygen to avoid complicating side processes such as reaction 9. Known concentrations of atomic oxygen in a nitrogen carrier are readily obtained by titrating active nitrogen with nitric oxide, according to reaction 1.

The addition of a small excess of nitric oxide makes it possible to follow, downstream, the decay of the atomic oxygen, by measuring the intensity of the air afterglow emission produced. Addition of hydrogen accelerates the oxygen atom decay by an amount proportional to $[O] \cdot [H_2]$, and measurement of the HNO emission from the reaction products shows that one hydrogen atom is formed for each oxygen atom removed. In fact, the OH radicals formed in reaction 7 are removed by the very rapid process

$$O + OH = H + O_2 + 17 \text{ kcal/mole}, \qquad (10)$$

which is discussed below. The rate of removal of oxygen atoms is therefore twice that of the initial-step reaction (reaction 7). The Arrhenius plot of k_7 in Fig. 4 shows that the line obtained from discharge-flow experiments passes very close to the point obtained by studying the hydrogen-oxygen reaction, and that the discharge-flow method gives a much more accurate temperature coefficient than could be obtained from studies of combustion reactions, where only a limited temperature range is accessible.

Hydroxyl radicals are readily obtained by the rapid reaction

$$H + NO_2 = NO + OH + 30 \text{ kcal/mole} \qquad (11)$$

The acceleration by molecular hydrogen of the decay of the OH absorption spectrum yields a rate constant for reaction 8, but the temperature dependence of k_8 needed for comparison with high-temperature systems is not yet available (*10*).

In the absence of molecular hydrogen, OH radicals decay quite rapidly (*5*, *10*) by the reactions

$$OH + OH = H_2O + O \qquad (12)$$

$$O + OH = H + O_2 \qquad (10)$$

The second of these reactions, mentioned above, is the reverse of the slow step (reaction 6) in the hydrogen-oxygen chain reaction. A value $k_{10} = 3 \times 10^{13}$ cm^3 mole^{-1} sec^{-1}, which is independent of temperature and corresponds to reaction at one collision in four between oxygen and OH, can be obtained in these systems. This agrees, to within a factor of 2, with the value of k_{10} at high temperatures, calculated thermodynamically from measurements of k_6 in the hydrogen-oxygen reaction (*5*).

Finally, reaction 9 can be studied by adding molecular oxygen to hydrogen atoms in an argon carrier and using HNO emission to observe the accelerated decay of hydrogen atoms. The carrier technique, in which a little hydrogen in an argon carrier is passed through the electric discharge, eliminates side reactions which would occur if large amounts of molecular hydrogen were present. The system is complex, since the rapid subsequent step

$$\begin{aligned} H + HO_2 &= OH + OH \\ &= H_2O + O \qquad (13) \\ &= H_2 + O_2 \end{aligned}$$

has three parallel paths, and reactions 12 and 10 can also occur. Nevertheless, values of k_9 can be obtained (at, and below, room temperature) which, when extrapolated, agree very well with explosion-limit studies on the hydrogen-oxygen reaction (*5*).

Such methods can readily be extended to the reactions of oxygen, hydrogen, OH, and so on, with simple hydrocarbons, aldehydes, and other compounds which are important in hydrocarbon combustion and in radiolysis. In the upper atmosphere, oxygen atoms, produced by the solar irradiation of oxygen and ozone, undergo the reactions

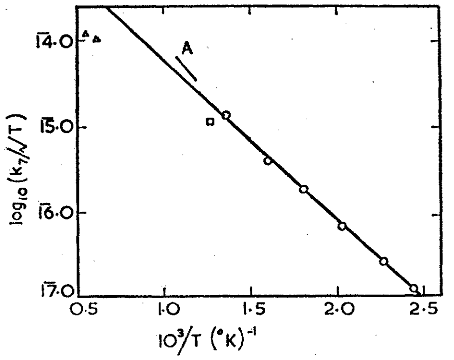

Fig. 4. Arrhenius plot for reaction 7. (Open circles) The points from discharge-flow experiments; (square) a point obtained for the hydrogen-oxygen reaction; (triangles) points from flame studies; (line *A*) points from the effect of hydrogen on the carbon monoxide, oxygen reaction.

$$O + O_2 + M = O_3 + M$$

$$O + O_3 = O_2 + O_2$$

Atomic hydrogen is also present, and catalyzes the decomposition of ozone:

$$H + O_3 = HO + O_2$$

$$O + OH = H + O_2$$

These reactions and many others can be studied in discharge-flow systems in the laboratory.

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