has tried to answer the questions how to generate trapped radicals, how to identify the active species present, how to measure their concentration, and how to recover them from the solid. None of these questions has been completely answered at this time.

Generation of trapped radicals

In general, trapped radicals can be prepared in two ways: by generating the radicals in the gas phase and suddenly freezing them in a solid matrix at low temperatures or; by irradiating the appropriate solid with either ultraviolet light or ionizing radiation. Both methods have been used extensively. The generation of radicals in the gas phase has usually (and more successfully) been done by electric discharge although both photolysis and pyrolysis of the gases have been employed. Both methods give similar results although each presents problems. When an activated gas is condensed, even at very low temperature, it is almost impossible to remove the energy from the gas completely at each collision of a gas molecule with the wall. The result is that the radicals strike the wall many times before being trapped in the solid, and a large number of them will be removed by chemical reaction. Further, diffusion may occur within the matrix or on the surface with resulting loss of radicals by recombination.

Radicals are usually formed by breaking chemical bonds, and thus they will normally be formed in pairs. If the radicals are formed by irradiation or photolysis of a solid, they will be trapped in pairs in a cage and will recombine immediately. It is only when there is an opportunity for diffusion so that some radicals can escape from the cage, but without enough energy to reach a second radical, that that radiation can successfully produce stabilized radicals. In both methods, wherever two radicals recombine a great deal of heat is liberated and the matrix in the neighborhood will be softened and melted. If other radicals are close by, they will have an opportunity to diffuse together and react. In this way an energy chain can be initiated causing the entire system to react very rapidly. Thus, as will be discussed later, the problem of trapping radicals in high concentrations is a very difficult one and has not yet been solved.

Identification

The identification of trapped radicals presents many serious problems, and, as a consequence, only a few have been convincingly identified. The difficulties are obvious. First, one can never be certain that only one active species is present and, in fact, one can imagine few systems where this would be true. Second, almost no data exist on the effect of the crystal field upon the radical trapped in it. The principal means of identifying radicals trapped in solids have been emission, infrared absorption, and electron spin resonance spectra. Chemical evidence has also been employed, but not always successfully.

The free radical systems that have been subjected to the most extensive investigations have been hydrogen, nitrogen, oxygen, NH, and methyl. When hydrogen gas containing H atoms is condensed at 4°K only a very weak glow is observed in the gas near the solid and none in the solid itself (16). No absorption bands can be detected in the near infrared. Thus, there is no spectral evidence for trapped H atoms. H atoms have

(22). Livingston irradiated solidified aqueous solutions of several acids with gamma rays from cobalt-60 at 77°K, and Matheson and Smaller performed similar experiments with ice. Both groups measured the electron spin resonance of the irradiated solid and found spectra characteristic of hydrogen atoms, Table 1. The measurements on ice, however, gave line

Table 1. Identification of trapped hydrogen atoms.

RADICAL	MATRIX	T°K	METHOD
H, D	H_2	4	esr
H	Ice ?	77	esr
H, D	H_2O-H_2SO_4	77	esr
H	CH_4	4	esr

separations much smaller than those in the gas phase or in the acid-water mixture. The discrepancy has not been satisfactorily explained.

Nitrogen atoms have undoubtedly been the most intensively investigated
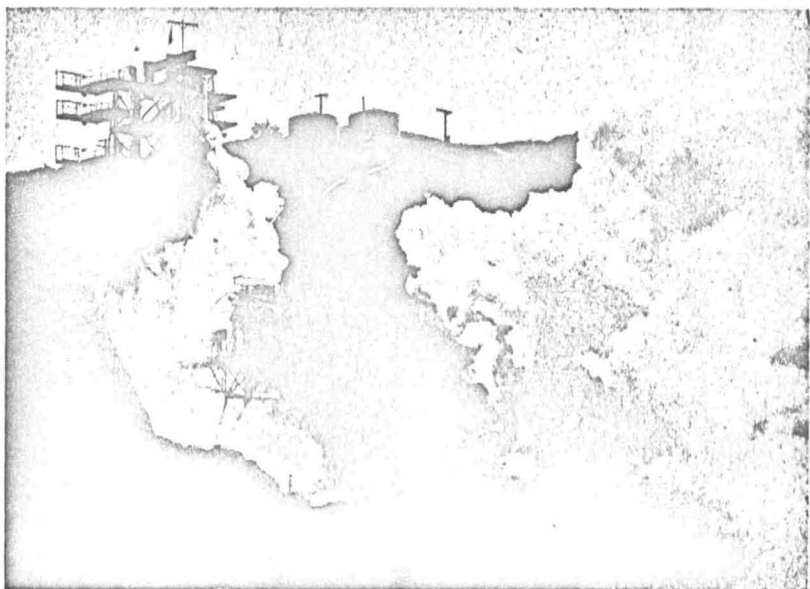
Remote at present, free radicals may yet be used for future propulsion.

been trapped in very low concentration in a hydrogen lattice and have been positively identified by Jen et al. (17, 18) using electron spin resonance. Hydrogen atoms gave a typical doublet and deuterium a triplet, similar to the spectra obtained in the gas phase. There has also been considerable speculation as to whether the hydrogen and deuterium atoms were trapped as H_3 or D_3. Some electron spin resonance data (18) suggest this possibility but are inconclusive. Attempts to predict the spectrum of H_3 from a priori theoretical considerations have also been inconclusive (19).

Some interesting measurements have been made by Livingston (20, 21) and by Matheson and Smaller

of any trapped radical. Unfortunately, some of the published material is conflicting, and final explanations of most of the phenomena have not as yet been adduced. The principal energetic species present in the nitrogen afterglow is atomic nitrogen in the ground (^4S) state (23), and in most of the studies discussed here the N atom concentration is in the order of 2% (23, 24, 25). However, small amounts of nitrogen in both the ^2D and ^2P states are present (26), their concentrations being, perhaps, 1% of that of the ground state N. The principal spectrum observed in the nitrogen afterglow is due to the B^3II_g——

——$A^3\Sigma u$ transition of molecular nitrogen which in turn arises somewhat