to a single free radical. Gibson *et al.* (*45*) and Ingram and Symons (*46*) have irradiated several alcohols fixed in a water-H_2O_2 glass with 2537 Å mercury radiation. Apparently the hydrogen peroxide was decomposed to OH radicals which then abstracted hydrogen from the alcohol leaving a free radical which was identified by its spin resonance spectrum.

Concentration in the matrix

It is evident from the above that the problem of identifying trapped free radicals with certainty is a complex one which has been solved satisfactorily in only a very limited number of cases. The problem of determining the number or concentration of trapped radicals is even more difficult since it involves not only identification, but measurement of the numbers involved. The most satisfactory methods for measuring concentration have been magnetic, employing either spin resonance or magnetic susceptibility. In his studies of hydrogen atoms, Livingston (*47*) estimated the hydrogen atom content of the irradiated frozen aqueous solutions of acids to be in the order of 0.1%. He also collected the hydrogen evolved upon warming the mixture and got satisfactory agreement with the spin resonance measurements. Matheson and Smaller (*22*) estimated the hydrogen atom content of irradiated ice to be of the order of 0.05 mole %, and from dipolar broadening, Jen *et al.* (*18*) estimated that the hydrogen atom content of the lattice was about 0.01%. In neither case were efforts made to maximize the hydrogen atom content and so the results given are not necessarily limiting.

Perhaps the most convincing measurement of the concentration of nitrogen atoms in a solid deposited from the nitrogen afterglow has been made by Fontana (*48*) who measured the magnetic susceptibility of the solid during deposition. He found that the nitrogen atom content built up slowly to concentrations as high as about 0.5%. Near this concentration the situation became unstable and a characteristic yellow flash occurred, at which point the temperature rose and the nitrogen atom content dropped precipitously. The atom content would then slowly build up until the unstable situation was again reached. Wall *et al.* (*43*) have estimated the nitrogen atom content of gamma irradiated solid nitrogen to be about 0.1%. Other, and much less reliable methods, have led to values as high as 4 to 6% (*49*). However, these higher values came from measurements of total heat release. Because this heat might have come from excited molecular species, the analysis should be taken with serious reservations.

Estimates of oxygen atom content in the solid condensed after passing oxygen through an electric discharge have led to values as high as 11%. It must be emphasized, however, that oxygen atoms have never been positively identified in the solid and the methods used for estimating their concentration are indirect and extremely doubtful. Thus, calorimetric methods (*49*) lead to oxygen atom contents of the order of 6%, and interpretations based upon the formation of ozone (*33*) have led to values in the order of 11%. The calorimetric method is questionable because of the possibility that the heat released came from sources other than atomic oxygen, and the high value of 11% obtained by inference from chemical reaction is probably of no value since infrared spectra have shown that no change in ozone content occurred during warm-up of the solid (*50*).

Wall *et al.* (*43*) found both methyl radicals and hydrogen atoms upon irradiating methane with gamma rays from cobalt-60 at 4°K. The total radical content of the solid was estimated, by electron spin resonance methods, to be of the order of 0.08%. Upon warming, the hydrogen atoms disappeared more quickly than the methyl.

From the above it is evident that the best data uniformly point to very low free radical contents. This is especially disappointing to those interested in the use of trapped radicals as jet fuels. It should not be surprising since it is necessary that the radicals be separated by a rigid matrix if they are to be prevented from recombining and since any recombination is probably sufficient to set off a chain reaction, resulting in the disappearance of essentially all of the radicals. Statistical studies have been made by Jackson and Montroll (*51*) and Golden (*52*) in an effort to ascertain the probability of laying down an array of radicals on sites that would be sufficiently isolated from other radicals to be stable. The results have shown a maximum of about 10-15% radicals in the solid. A more sophisticated treatment by Jackson (*53*), employing a model based on autoignition, has deduced a maximum nitrogen atom content of about 0.3%, in good agreement with the value obtained experimentally by Fontana (*48*). Thus, it seems doubtful at this time that there are any reasonable prospects of obtaining high concentrations of radicals in the near future.

J. L. Franklin was appointed to the post of research associate at Humble Oil & Refining when it was established in 1947. He recently spent eighteen months with NBS, as guest scientist on the free radicals project. Franklin has published in the fields of reaction kinetics, thermodynamics and electron impact phenomena. He is now on the advisory board for a new series of reference books on Advances in Petroleum Chemistry and Refining. A member of the Farady Society, ASTM, and a fellow in the Physical Society, he is also a former chairman of A.I.Ch.E.'s South Texas Section.

The effect of matrix material upon the stabilization of radicals has not been established although there have been small advances made in this field. In general, the higher the melting point, or the higher the energy of vaporization of the matrix material, the more effective is the matrix in stabilizing radicals. This was indicated above in the effect of hydrogen, nitrogen, and methane on the hyperfine splitting of nitrogen atoms (*17, 18*). It has also been observed by Pimentel and his colleagues (*54, 55*) who found that stabilization increases in the order nitrogen, argon, krypton, and xenon as would be expected from their melting points and heats of vaporization. However, there are essentially no data on the stabilization of radicals in strongly-bound matrices such as might be expected of water. An exception has been noted in the studies of irradiation of ice and aqueous solutions of acids at 77°K, where small concentrations of hydrogen atoms were trapped. It is interesting that in Wall's studies of irradiation of methane, the hydrogen atoms disappeared at temperatures far below 77°K. Glasses have been used in several studies and have been found to be effective in trapping radicals, but no systematic study of their effectiveness has been made. It is evident that much work still needs to be done to define the effect and mode of action of the matrix in trapping radicals.

Recovery of trapped radicals. Very little has been done to develop methods of recovering radicals from a matrix. In fact, the author knows of only one brief paper on this subject. Broida and Peyron (*56*) collected the glowing nitrogen solid at 20°K then let the solid warm slightly and distill to an adjacent surface at about 1.2°K. The redistilled solid, collected at the lower temperature, showed the characteristic spectral lines of the ^2D-