these experiments promises to be of general application to the spectroscopic study of photosensitized reactions.

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## Krypton Diffusion in Scintillation Counter Plastic

THE determination of radioactive krypton in the atmosphere, as carried out by the Radiological Sciences Laboratory, New York State Department of Health (private communication from N. Irving Sax), involves extraction and concentration of krypton, then injection of this into a vial containing chips of a scintillation counter plastic, such as $p$-terphenyl in polyvinyltoluene commercially available from Pilot Chemicals, Massachusetts. By scintillation counting, this procedure measures extremely low levels of the $\beta$ emitter, 10·76 yr krypton-85.

One possible source of error, seldom considered, is the diffusion of the gaseous krypton being measured into the solid plastic, and its retention there. To evaluate this, measurement was made over a temperature range of the permeation rate, diffusion constant and solubility of normal krypton in the polymer. The rates for the most abundant isotope, krypton-84, were determined by mass spectrometry. These values will be extremely close to those for radioactive krypton-85. The quantum isotope effect in permeation is small and measurable only in the light isotopes $H_2$ and $D_2$, as found by Frisch and Rogers[1].

The mass spectrometric method of permeation measurement is described in refs. 2 and 3 in detail. The clear polyvinyltoluene polymer, $10\cdot6 \times 10^{-3}$ in. thick, was vacuum degassed in a permeation cell. Then 200 mm of krypton was put on the high side with the low side leading directly to the mass spectrometer. This was a single focusing 60° machine, of 6 in. radius, made by General Electric. This method enables extremely low flow rates to be found unambiguously. By measuring the height of peak 84 at steady state flow, the rate of krypton permeation was determined. The lag time to steady state enabled the diffusion constant to be measured[4].

The units of the permeation rate $P$ are: cm³ gas (STP) s⁻¹ per cm² area per mm thick per 1 cm Hg gas pressure difference. The diffusion constant $D$ is in cm² s⁻¹ and the solubility of the gas in the polymer is in cm³ (STP) gas per cm³ polymer for 76 cm Hg applied gas pressure. The results are given in Table 1.

Table 1. KRYPTON IN SCINTILLATION POLYMER POLYVINYLTOLUENE

| °C | Permeation rate $P$ | Diffusion constant $D$ | Solubility $S$ |
|---|---|---|---|
| 25 | $4\cdot2 \times 10^{-10}$ | $4\cdot3 \times 10^{-9}$ | 0·75 |
| 50 | $1\cdot5 \times 10^{-9}$ | $2\cdot4 \times 10^{-8}$ | 0·50 |
| 75 | $4\cdot8 \times 10^{-9}$ | $1\cdot0 \times 10^{-7}$ | 0·37 |

With the units used, and assuming the diffusion constant is independent of concentration, as it probably is at these low values, the solubility $S = 7\cdot6\ P/D$.

From plots of log $P$ and $D$ against $1/T$, the activation energy can be determined for the processes. For permeation of krypton in the polymer it is 10,000 calories, and for diffusion 13,000 calories.

The time lag $L$ to establish steady state flow to vacuum through a $10 \times 10^{-3}$ in. sheet of polymer can be calculated from $L = d^2/6D$, where $d$ is the polymer thickness in cm. At 25° C this lag is 7 h. If there is krypton on both sides of a degassed sheet, the time to half saturate the sheet can be computed from tables given by Newman[5] and Norton[6]. It amounts to 5 h. Hence, if the plastic is exposed to krypton-85 for the order of two or three hours during the scintillation measurements, the dissolved gas remaining in the plastic can become important. At an equilibrium pressure of 1 atm, the volume of gas held in the plastic at 25° C is almost the volume of the plastic itself. The time for desorption is about the time for take-up. For precise measurements this gas must be desorbed and pumped away before the next sample is introduced. It is most advantageous from the standpoint of gas solubility to keep the exposure time of the plastic to the gas at a minimum, and to allow sufficient time, with sweep-out, between measurements.

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## Growth of Crystals in Silica Gel using a Co-solute

AFTER the publication by Cochrane[1] of a procedure for growing single crystals of $\beta$-AgI in concentrated KI solution, several workers[2,3] described the application of variants of his technique to growth in silica gel. We have also been active in this area and have grown single crystals of $\alpha$-HgS and $\beta$-HgS as well as $\beta$-AgI, AgBr and AgCl.

The general feature of this method is the existence of some soluble material which itself increases the solubility of the material of interest in a nonlinear fashion with concentration of the soluble material by complex formation in solution, or by formation of a soluble double salt. In the crystal growth operation, the concentration of the combined solution is reduced by diffusion into the gel. Because the solubility of the material is a nonlinear function of the concentration of the soluble material, it may reappear. In the case of HgS the aqueous solubilities of $\alpha$-HgS and $\beta$-HgS are known[4] to be enhanced by the presence of $Na_2S$. Similarly, the solubilities of the various silver halides are known to increase by many orders of magnitude in concentrated alkali halide and alkaline earth halide solutions as well as in silver complex formers like $Na_2SO_3$, $Na_2S_2O_3$, and others.

We have grown small crystals ($\sim 0\cdot5$ mm max.) of both $\alpha$-HgS and $\beta$-HgS in silica gels from $Na_2S$ solution under varied $pH$ and temperature. Typically, sodium silicate gels of specific gravity 1·05 in the $pH$ range 5·8–8·5 were formed with nitric acid and allowed to stand overnight. A solution of $Na_2S$–HgS was then added to the top of the gel. In a matter of a day, crystals appeared in the gel near the interface and in the top solution. Severe gel shrinkage was evident and dilution of the top solution by the syneresis liquid from the gel was thought to be the principal reason for this crystal formation in the top solution. Initially, only cubic, black $\alpha$-HgS crystals were evident, but after standing for several days conversion to the red hexagonal $\beta$-HgS occurred. The rate of conversion