S **83.** *Self-diffusion in Some Solids.*

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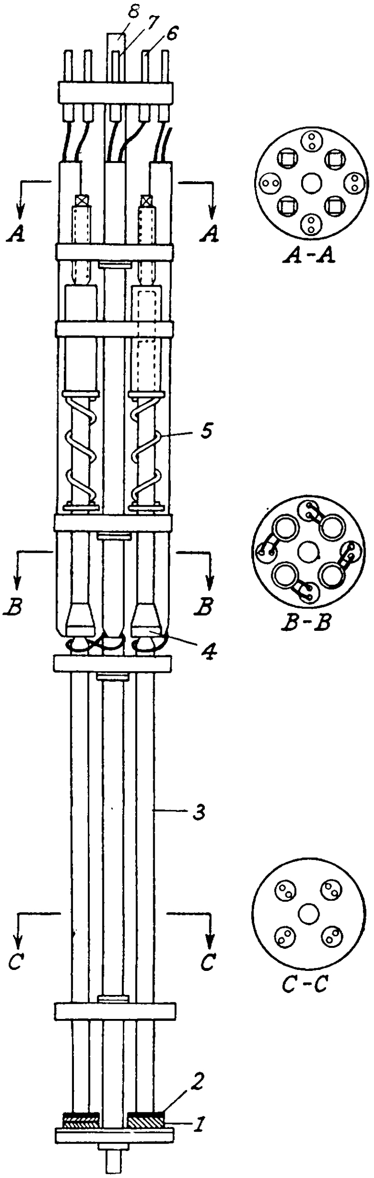
A preliminary account is given of experiments in which radioactive tracers have been used to determine self-diffusion constants.

STUDIES of the mechanism of reactions in solids necessitate measurements of diffusion constants. In the case of self-diffusion the principal methods use radioactive tracers. Some work on this field has been done in Professor Hedvall's institute in Gothenburg. The methods chiefly used are the following :

FIG. 1.



(1) A pellet is made of two layers of equal thickness, one of which is radioactive. When diffusion takes place, a decrease of the activity on the active surface and an increase in that on the other (initially inactive) surface can be measured. Thus two values for the diffusion coefficient can be obtained.

(2) A thin active layer is allowed to diffuse into the inside of a pellet and the decrease in activity is measured. This was Hevesy's original idea and has been applied to β-ray-emitting substances in England by de Hevesy and MacKay, in the U.S.A. by Steigman and Banks, and in Australia by Anderson.

(3) A radioactive pellet is pressed against an inactive pellet. At high temperatures diffusion takes place and the two pellets sinter together, but they can be separated at the original surface of contact. The amount of activity diffused into the formerly inactive pellet yields a value for the diffusion coefficient.

The systems dealt with hitherto have been chosen partly on account of their technical importance, and partly on account of their interest for reactions in the solid state. A few applications of methods (2) and (3) are described below.

Method (2).—The thin layer will usually be produced by condensation of the substance which has been evaporated in a vacuum. Sometimes this method is difficult to use, *e.g.*, in the case of lime. In such a case, we used a form of precipitation method. The pellet is brought in contact with a solution of ammonium carbonate and "impregnated" that way. If this surface is placed in a solution of radioactive calcium chloride, a thin layer of radioactive calcium carbonate will be formed. This layer is easily transformed into lime by heating the pellet to about 1000°. It has, however, not yet been proved that this method is as reliable as condensation in a vacuum.

Method (3).—For the " contact method " we use the small apparatus shown in Fig. 1. It contains at (1) three pairs of pellets and a compact one of double thickness. All pellets are kept between platinum foils which have been pressed on already in the die, and the pressure in the holder acts on the pellets by means of a platinum plate (2) which at the same time acts as the hot junction of a thermocouple. The leads of the thermocouple are contained in a double-holed protection tube of quartz (3) on which pressure is exerted at (A) by means of springs at (5).

The thermoelectricity may be measured between (6) and (7)—for the pair of pellets shown on the left—and the electrical conductivity is measured between (7) and the central bar (8). The latter measurement is made in order to control the amount of contact between the two " diffusion pellets " by comparing their electrical resistance with that of the compact pellet which is as thick as the two " diffusion pellets " together. A correction for imperfect contact can be made when calculating the diffusion values.

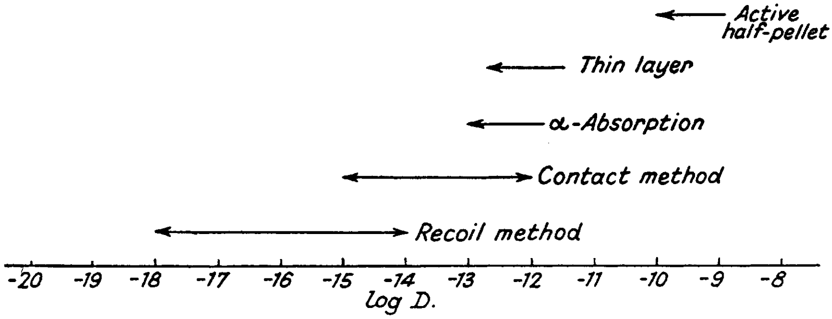
The whole apparatus can be placed in a tube of Pyrex, Supremax, or quartz, and can thus be kept in a vacuum or a defined gas atmosphere.

After being heated for a certain time to the temperature of diffusion, the pellets are separated and the contact surface of the originally inactive pellet is measured with a Geiger–Müller counter. The activity taken up by that pellet follows the equation $S = qC\sqrt{Dt/\pi}$, where q = surface of contact, C = concentration in impulses/cm.^{3}, D = diffusion constant, and t = the time, and thus a value for the diffusion constant can be obtained.

With sufficiently high temperatures it is possible to get several values with one pair of pellets. At lower temperatures, at least the first values of all pairs, separated at different times, fit into the theoretical curve.

This method has been applied to lead salts, and some preliminary values with lead iodide are in fair accordance with those obtained by Seith by the method of radioactive recoil. It might be mentioned that the contact method fills the gap which has hitherto existed for measurement of diffusion constants between 10^{-12} and 10^{-14} cm.^{2}/sec., as may be seen in Fig. 2, which reproduces the range of sensitivity for different methods of diffusion measurement.

FIG. 2.



Measurement of self-diffusion in solids with radio-tracers.

Silver sulphate. The constant of self-diffusion has been measured between 250° and 650° and, up to the transition point (assumed hitherto to be 411°), has been found to be in fairly good agreement with values calculated from the electrical conductivity measured by Jagitsch (*Trans. Chalmers Univ. Techn., Göteborg*, 1942, No. 11). That indicates that the diffusion is due to the migration of ions, and processes of direct exchange between neighbouring lattice sites are not present in larger amounts.

Lead oxide. The contact method yielded values of the order of magnitude of 10^{-14} cm.^{2}/sec. to 10^{-12} cm.^{2}/sec. between 485° and 570°.

Zinc oxide and $ZnO{\cdot}Fe_2O_3$. These systems are of interest in connection with the formation of zinc–iron spinel. The self-diffusion of zinc in the spinel has been found to be higher than in the pure zinc oxide. The exact values will be published later.

Calcium silicate. The diffusion of calcium in the system $CaO–SiO_2$ is slow, in accordance with Jander's theory of formation of calcium silicates (*Z. anorg. Chem.*, 1934, **218**, 211).

Investigations on the mobility of calcium in the different silicates are in progress.

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