S **82**. *The Self-diffusion of Silver and Mercury in* Ag_2HgI_4.

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Two methods for the determination of self-diffusion coefficients by means of radioactive tracers are discussed. Preliminary experiments are described in which these methods are applied to the species named in the title.

Reactions in solids are usually determined by the rate of diffusion of the reacting particles. Values for self-diffusion coefficients at one time could be determined only from the electrical conductivity and the transference numbers, but not by a direct measurement, except in the special cases where natural radioactive isotopes of the diffusing particles were available. After the discovery of artificial radioactivity, however, a great number of tracers became available for studying self-diffusion processes in solids. To get a confirmation of Wagner's theory (*Z. physikal. Chem.*, 1936, **34**, *B*, 309) of the reaction mechanism in the system AgI–Ag_2HgI_4–HgI_2, an investigation was started of the self-diffusion coefficients of silver and mercury in their respective iodides and in Ag_2HgI_4 as a function of the temperature, radioactive silver and mercury being used. Some of these coefficients have been calculated before from electrical measurements, and thus it is possible to control the reliability of this conversion.

The radio-nuclides ^{111}Ag and ^{203}Hg were used, both of which emit electrons with a rather low energy. It is therefore convenient to use this property, *i.e.*, the high absorption of the radiation, in determining the diffusion rate. This can be done in two ways.

(I) The first method, used by Anderson and Rickards (*J.*, 1946, 537) and by Steigman, Shockly, and Nix (*Physical Rev.*, 1939, **56**, 13), is as follows: A very thin layer of active salt is deposited by evaporation on a pellet of inactive material which is very thick in comparison with the diffusion length. By measuring the decrease in β-ray activity from the sample due to the diffusion of the radio-nuclide it is possible to determine the self-diffusion coefficient. According to Fick's law, the following equation corresponds to the case of diffusion from an infinitely thin layer along an infinite cylinder:

$$C = \frac{Q}{\sqrt{\pi Dt}} \exp(-\,x^2/4Dt)$$

where $C \equiv$ concentration at a distance x from the original surface after a time t, $D \equiv$ diffusion coefficient, and $Q \equiv$ amount of diffusing material originally deposited, *i.e.*, the activity of the pellet measured before the diffusion. At the end of the experiment the activity A (in counts/min.) can be calculated from the absorption law:

$$A = \int_0^\infty C \exp(-\mu x).\mathrm{d}x$$

where $\mu \equiv$ absorption coefficient. The solution of the integral is

$$A/A_0 = \exp(\mu^2 Dt).[1 - \Psi]$$

$$\Psi = \frac{2}{\sqrt{\pi}} \int_0^{\mu\sqrt{Dt}} \exp(-\xi^2).d\xi$$

If the value of A/A_0 is plotted against $\mu\sqrt{Dt}$ it is possible to evaluate the diffusion coefficient if t and μ are known.

(II) If the diffusion rate is high ($D > 10^{-8}$ cm.^{2}/sec.) or if, for some reason, it is impossible to get a thin layer of active salt upon the inactive pellet, method (I) cannot be used. It is then possible to let the active material diffuse from a layer of thickness h into a cylinder of thickness d. This method may be said to be a modification of that of Stefan and Kawalki but has the advantage that one is working with only one pellet. Consequently, there are no contact surfaces and no contact resistances. The change in β-activity due to the diffusion of the tracer atoms into the inactive part of the pellet is observed. The diffusion equation can be solved for these boundary conditions, and if C_0 is the tracer concentration between $x = 0$ and $x = h$ at time $t = 0$, the following result is obtained:

$$C/C_0 = \frac{h}{d} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \exp[-(n\pi/d)^2 Dt].\cos\frac{n\pi x}{d}.\sin\frac{n\pi h}{d}$$

After time t the activity of the originally active surface is $\int A_1 = \int_0^d C.\exp(-\mu x)\mathrm{d}x$, hence

$$A_1 = C_0\left(\frac{1 - \exp(-\mu d)}{\mu}.\frac{h}{d} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\exp[-(n\pi/d)^2 Dt]\sin\frac{n\pi h}{d}.\frac{1 - \exp(-\mu d)\cos n\pi}{\mu[1 + (n\pi/\mu d)^2]}\right)$$

The activity of the originally inactive surface can be obtained in the same way:

$$A_2 = \int_0^d C.\exp[-\mu(d - x)]\mathrm{d}x, \text{ hence}$$

$$A_2 = C_0\left(\frac{1 - \exp(-\mu d)}{\mu}.\frac{h}{d} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\exp[-(n\pi/d)^2 Dt]\sin\frac{n\pi h}{d}.\frac{\cos n\pi - \exp(-\mu d)}{\mu[1 + (n\pi/\mu d)^2]}\right)$$

C_0 can be determined from the activity of the pellet before the diffusion. This activity being A_0, the absorption law gives

$$C_0 = \mu A_0/[1 - \exp(-\mu h)]$$

Consequently, if μ and C_0 are known, A_1 and A_2 can be determined as functions of Dt/d^2 for certain values of μd. The diffusion coefficient can be obtained first from the decrease of activity on the active side, and secondly from the increase of activity of the inactive side. The method is not as sensitive as the first one, but the sensitivity can be varied within rather wide limits by changing the thickness of the pellet.

Obviously, a fairly accurate value of the absorption coefficient μ of the β-radiation is important for the determination of D. The measurement of μ offers great difficulties because it is not easy to get layers thin enough with respect to the soft radiation. Two methods have been used. By the first, a small amount of active salt is evaporated on to a thin metal plate and then thin layers of inactive salt are added in the same way. The thicknesses of the layers are determined by weighing. The other method consists of evaporating a very thin active layer on an inactive pellet which is as thin as possible. The activity is measured (A_0), and the pellet is heated until the radio-nuclide is evenly distributed. If the activity is now A and the thickness d, the absorption law gives

$$A/A_0 = [1 - \exp(\mu d)]/\mu d$$

From this μ can be calculated. Measurements of the absorption coefficient in different materials are in progress but have not yet been completed. The value used for ^{111}Ag is $\mu = 15{\cdot}3$ cm.^{2}/g., and for ^{203}Hg, $\mu = 77$ cm.^{2}/g.

The heating was done in nitrogen purified from oxygen. A thermostat was used for temperatures below 125° (±0·1°), and an electrical furnace for higher temperatures (±1°). The activity of the pellets was measured by a Geiger–Müller counter as the difference between the total radiation and the γ-radiation, which amounts to only a few units %.

The results obtained are shown in Figs. 1 and 2, where also those values of the diffusion coefficients determined from electrical conductivity are reproduced.

FIG. 1.

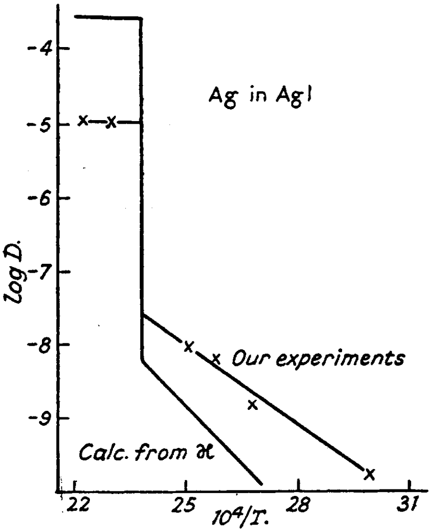
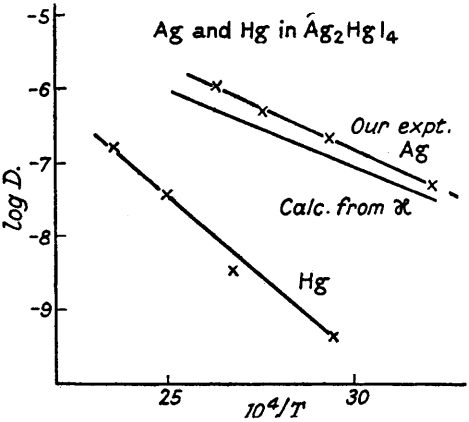


FIG. 2.



AgI (Fig. 1).—At temperatures lower than 147° (α-AgI), D has been determined by method (I), and for higher temperatures by method (II). We cannot yet give any explanation for the difference in the slopes and in the absolute values of the curves. Further investigations are proceeding.

Ag_2HgI_4 (Fig. 2).—D_{Ag} and D_{Hg} have been determined by method (I) or (II) according to the temperature (as above). The agreement in the values for the self-diffusion of silver determined from the electrical conductivity is here rather good.

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