24. *Investigation of hydrogen motion in liquids by neutron radiography*

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The diffusion of hydrogen into deuterated liquids was observed using the direct exposure method. Measurements on H_2O-D_2O diffusion in temperature intervals from 0°C to 45°c are in good agreement with the literature. The results indicate a somewhat concentration-dependent diffusion coefficient. Measurements on CH_3OH-CD_3OD and CH_3OD-CD_3OD indicate that the methanol molecule diffuses as a whole.

1. As is well known, hydrogen can easily be detected using neutron radiography (ref. 1, 2). This offers many useful applications, for example, investigations of metal adhesion, the detection of hydrogen behind thick metal plates and the diffusion of hydrogen. First measurements on these subjects made earlier at the Atominstitut (ref. 3) included the diffusion of hydrogen Zirconium and the diffusion of H_2O D_2O. In continuation of these experiments further measurements on H_2O-D_2O and measurements on methanol have been performed. The experimental setup was the same as before. A conical collimator gives a neutron beam with 10 min divergence. The neutron flux at the position of the converter screen was about 2.10^5 cm^2/s. The direct exposure method was applied, using a 25 µm thick Gd-converter and Osray DW film. The film density was measured with a microscope-photometer. To study the diffusion of H_2O-D_2O, the sample container was first filled with D_2O up to half its height. On top of this, H_2O was carefully poured. The sample container could be held at any constant temperature between 0°C and 40°C within ±0.1°C. The container was 12 cm high, 7 cm wide and had a thickness of 0.5 cm. The concentration profile was obtained by comparing the film density with density data obtained using a series of standard mixtures.

2. Radiographs were taken first in the temperature range between +5°C and +20°c and at different times (0 - 6 h) (Fig. 1). Attempts were also made to obtain radiographs below the melting point of D_2O (3.8°C). The result obtained is shown in Fig. 2, which indicates that the heavy water in this case was not frozen but undercooled. Stirring the water led to instantaneous freezing of the D_2O. The concentration profile at 20°C is shown in Fig. 3. From these curves the diffusion coefficient in the normal sense was obtained as the best fit to the concentration profiles of solutions of

$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} \qquad (1)$$

where c = concentration of D_2O

D = diffusion constant for the H-atoms which must not be confused with the diffusion coefficient of the whole water molecule).

3. The results of these investigations are in good agreement with values in the literature (refs.4-14) (Fig. 4). The low temperature values show a marked deviation from a straight line. The low diffusion coefficient here indicates a more stable type of short-range order in the undercooled D_2O. Because of deviations from the expected form of the concentration profiles attempts were also made to explain the data using a concentration-dependent diffusion coefficient. The diffusion equation in this case is

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left[D(c) \frac{\delta c}{\delta x} \right] \qquad (2)$$

with the initial conditions

$$c = c_o \quad \text{at} \quad x < 0$$
$$c = 0 \quad \text{at} \quad x > 0 \qquad (3)$$

Evaluating this equation according to Boltzmann (ref. 15) leads to

$$D(c) = -\frac{1}{2t} \frac{\int_0^c x \, dc}{\frac{\delta c}{\delta x}} \qquad (4)$$

4. The limiting condition for the validity of this equation is that the concentration variation must not have reached the ends of the diffusion medium. Using equation (4) the concentration-dependent diffusion coefficient can be evaluated from any of the concentration profiles at any time after the start of the diffusion process.

5. The evaluation for low concentrations is difficult for two reasons. First, measurement of the film density is most accurate in the region of maximum slope of the density curve, so that for the exact evaluation at small concentrations other exposure times or sample thicknesses should be used. Second, the absolute error in $\delta c/\delta x$ has most influence at low values of concentration, where it is also small (see equation (4)). A more detailed discussion is given elsewhere (ref. 16). Fig. 5 shows D(c) at a tempera-

ture of 20°C. A marked dependence of the diffusion coefficient of concentration results from the measurement. The minimum is near to 50% but rather on the D_2O side, which holds also for the other temperatures. A similar result was obtained by Adamson and Irani (ref. 17) using the diaphragm cell technique.

6. Further investigations were made on the diffusion of methanol. Using the experimental arrangement described above the mutual diffusion of CH_3OH-CD_3OD was studied. (Fig. 6). Afterwards measurements on CH_3OH-CD_3OD were made. The results agree well with the data obtained by Partington et al. (ref.10) on the diffusion of CH_3OH-CH_3OD (Fig. 7). This indicates that the methanol molecule diffuses as a whole.

7. The results presented here show that neutron radiography is a powerful tool for investigating the diffusion of hydrogen in different systems. Further work on the diffusion of H_2-D_2 and ortho-para-conversion is in progress.

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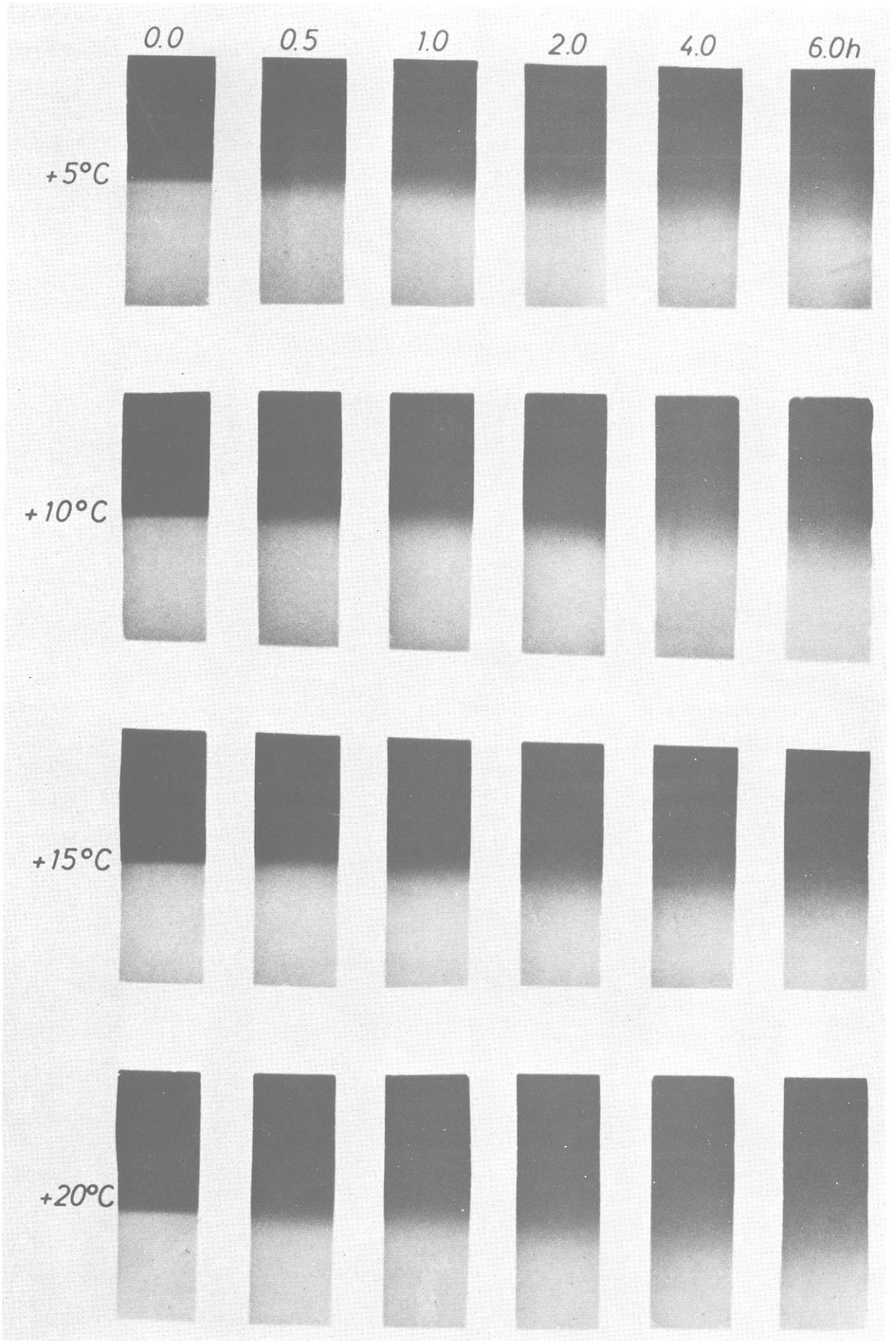

Fig. 1 Neutron radiographs of the H_2O-D_2O diffusion process at different times, at temperatures below the melting point of D_2O (positives).

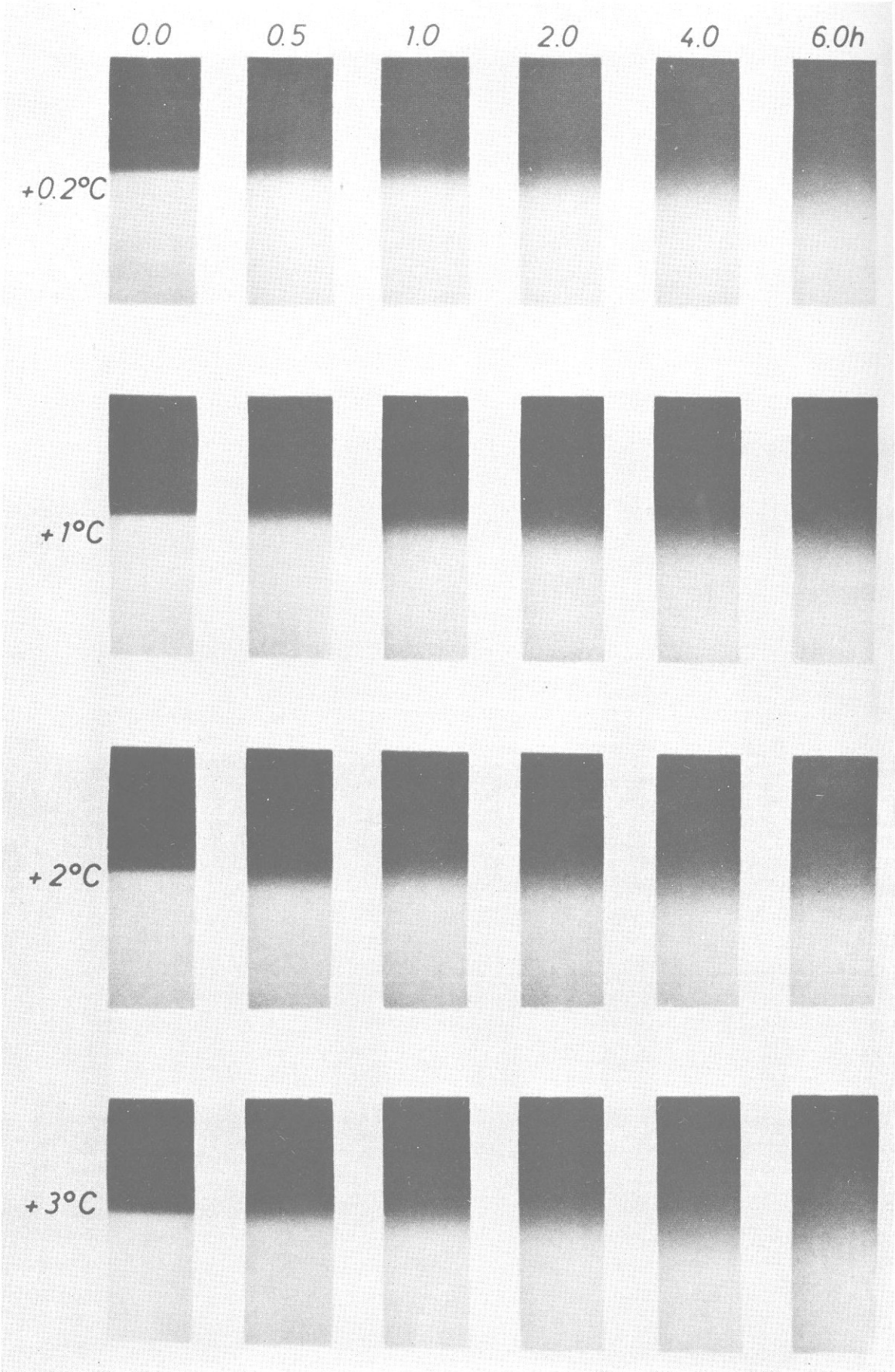

Fig. 2 Neutron radiographs of the H_2O-D_2O diffusion process at different times, at temperatures below the melting point of D_2O (positives).

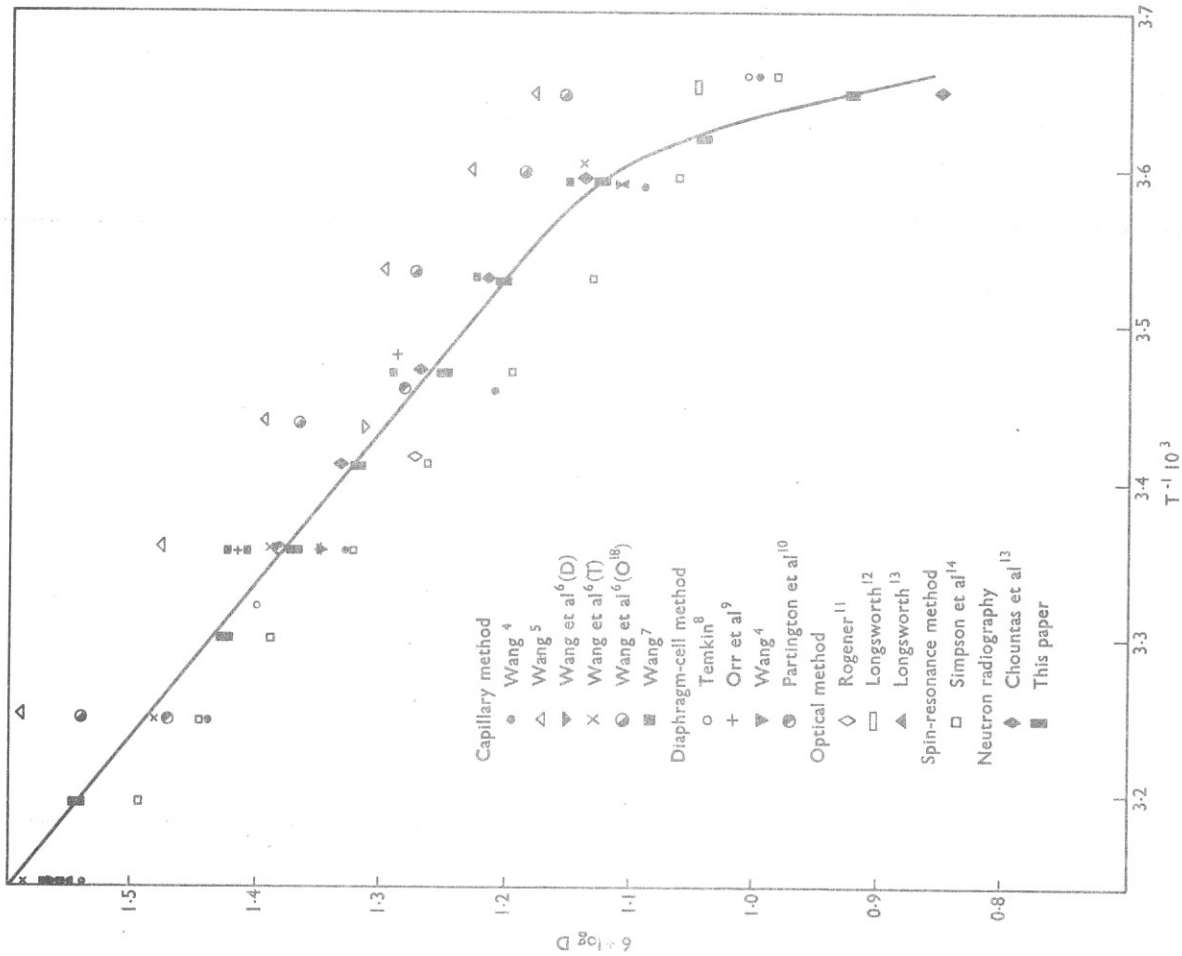

Fig. 4. Variation of diffusion coefficient of H_2O with temperature.

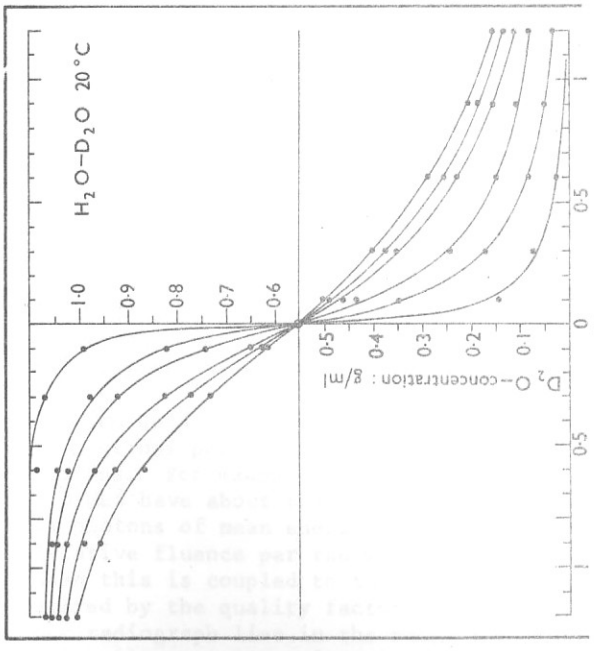

Fig. 3 Concentration profiles for H_2O–D_2O diffusion at 20°C (times as in Fig. 1).

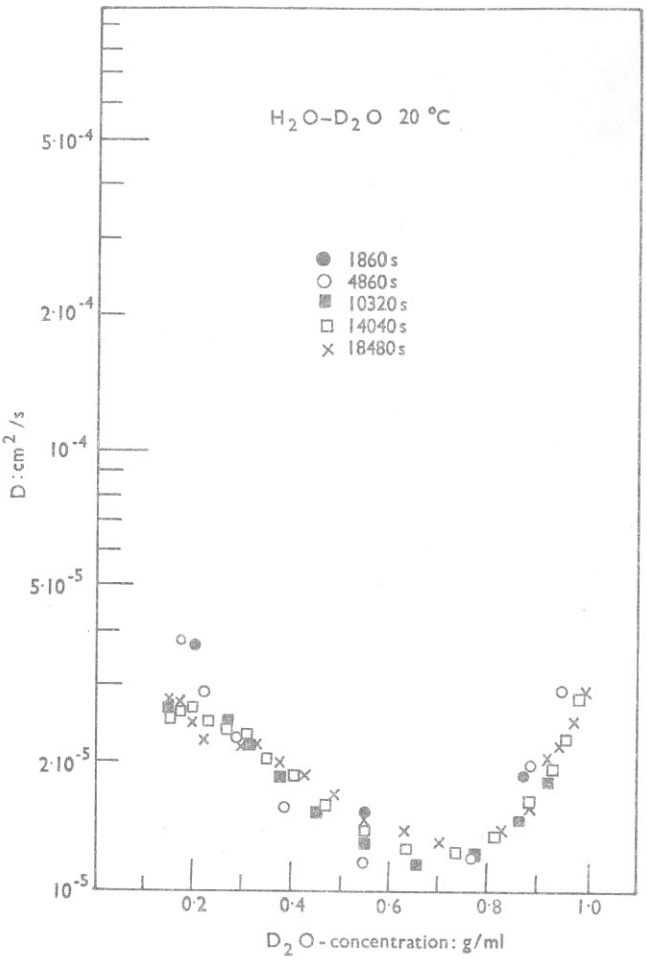

Fig. 5 Variation of diffusion coefficient of H_2O with D_2O concentration at 20°C. The times indicate from which concentration profile D(c) has been calculated.

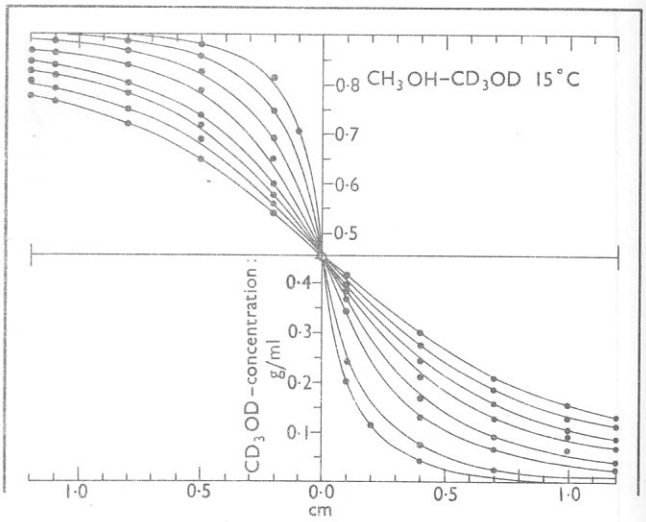

Fig. 6. Concentration profiles for CH_3OH-CD_3OD diffusion process at 15°C at times between 0 and 6 h.

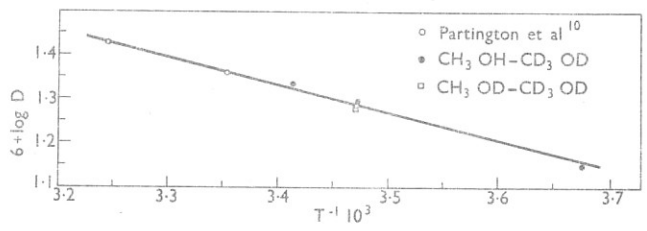

Fig. 7. Variation of diffusion coefficient of methanol with temperature

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