

Fig. 16. Diffusion coefficients for sulfate solutions at 0°C.

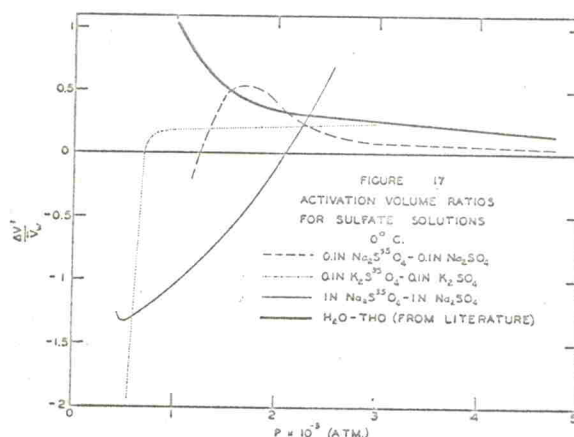


Fig. 17. Activation volume ratios for sulfate solutions at 0°C.

ratio to relatively small values (Fig. 17). Inasmuch as the activation volume ratios are extreme and their variations are compressed in the pressure range below 1000 atmospheres, only the high pressure values are plotted. It is this portion of the curves that indicate the formation of similarly stable structures for water and sulfate solutions.

The conductivity data of Zisman<sup>7</sup> on 0.01 *N* salt solutions (including Na<sub>2</sub>SO<sub>4</sub>) shows a maximum in the conductance at about 1000 atmospheres, followed by a

<sup>7</sup> W. A. Zisman, Phys. Rev. 39, 151 (1932).

linear decrease. The lack of detailed structure may be due to the decreased concentration or to the lack of sensitivity of conductance.

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## The Effect of Pressure on Diffusion in Aqueous and Alcoholic Salt Solutions\*

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Diffusion coefficients have been measured as a function of pressure to 10 000 atmos for the following aqueous solutions:

0.1 *N* Hg(NO<sub>3</sub>)<sub>2</sub> at 0°, 25°, 50°, 75°C,  
0.1 *N* CaCl<sub>2</sub> at 25°, 50°C,  
0.1 *N* Ca(NO<sub>3</sub>)<sub>2</sub> at 25°C,  
0.1 *N* TiNO<sub>3</sub> at 25°C,

and for 0.01 *M* HgCl<sub>2</sub> in *n*-butanol at 25° and 50°C. The results are interpreted in terms of the activation volume, and compared with previous data on water and sulfate solutions.

**D**IFFUSION coefficients have been measured as a function of pressure to 10 000 atmos in 0.1 *N* aqueous solutions of Hg(NO<sub>3</sub>)<sub>2</sub> at 0°, 25°, 50°, and 75°C; CaCl<sub>2</sub> at 25° and 50°C; Ca(NO<sub>3</sub>)<sub>2</sub> at 25°C; and TiNO<sub>3</sub> at 25°C. Measurements have also been made in a 0.01 *M* HgCl<sub>2</sub> in *n*-butanol solution.

In every case a radioactive tracer technique was used. The tracers (Hg<sup>203</sup>, Ca<sup>45</sup>, Ti<sup>204</sup>) were obtained from Oak Ridge National Laboratory of the U. S. Atomic Energy Commission. The salts were of cp quality. The *n*-butanol was purchased from Eastman Kodak.

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The experimental procedures, method of calculation of the diffusion coefficient, and the general theory have been previously discussed.<sup>1,2,3</sup>

The results are presented in Tables I-V and Figs. 1-5. These will be discussed under four headings; mercuric nitrate, comparison of nitrate isotherms, calcium chloride isotherms, and mercuric chloride-butanol isotherms.

<sup>1</sup> R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

<sup>2</sup> R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 575 (1953).

<sup>3</sup> Cuddeback, Koeller, and Drickamer, J. Chem. Phys. 21, 589 (1953).