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as superimposed on the factors that are influential in the case of water. Each of the three sulfate curves can logically be divided into three distinct sections, namely, from atmospheric pressure to the first minimum, from this point to the first maximum, and from this maximum onward to the highest pressure.

The minimum value for D occurs at 600 atmospheres for 1 *N* sodium sulfate, 1250 atmospheres for 0.1 *N* potassium sulfate and 2250 atmospheres for 0.1 *N* sodium sulfate. This decrease in D with initial application of pressure is normally expected, and molecular motion in this range involves, to a large extent, the pushing back of the surrounding medium as in normal liquids. It is evident from the slopes of the diffusion coefficient curves in this low pressure region that the ratio of activation volume to the molar volume of water,⁵ $\Delta V^\ddagger/\bar{V}_w$, (see Fig. 11) for the aqueous sulfate solutions is greater than for water and is positive. Within the sulfate solutions the initial activation volume ratio is

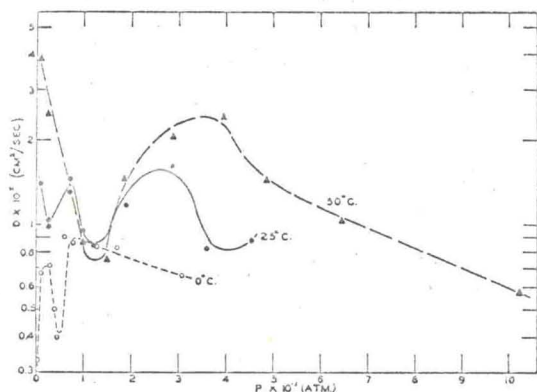


FIG. 9. Diffusion coefficients versus pressure 0.1 K₂SO₄.

largest for 1 *N* sodium sulfate followed by 0.1 *N* potassium sulfate and 0.1 *N* sodium sulfate, respectively.

As the pressure increases, the activation volume decreases and passes through a minimum, indicating that as the solution is compressed motion takes place preferentially by local collapse of the tetrahedral structure.

The activation volume ratio does not seem to be a function of the atomic volume of the cation, because the values for 0.1 *N* potassium sulfate lie between the values for 0.1 *N* and 1 *N* sodium sulfate, respectively. However, there is the possibility that a regular dependency of the activation volume ratio on the solvated volume exists which may be radically different from the corresponding atomic volumes of the cations.

In the second region, where D is increasing and the activation volume is negative, motion is apparently largely due to the local collapse of the structure.

In the pressure range beyond the last maximum value for D , the value of D decreases at a relatively slow rate while the activation volume ratio increases beyond zero for a short range, passes through a maximum, and

⁵ Hereafter this will be referred to as the activation volume ratio.

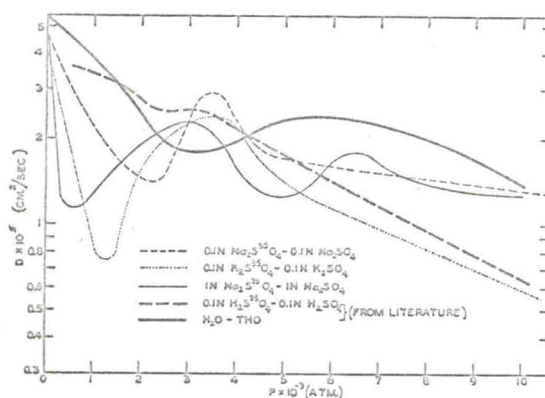


FIG. 10. Diffusion coefficients versus pressure sulfate solutions at 50°C.

then decreases at a decreasing rate which asymptotically approaches 0.08 for 1 *N* sodium sulfate, 0.10 for 0.1 *N* sodium sulfate, and 0.20 for 0.1 *N* potassium sulfate. These trends indicate that either the tetrahedral structure is completely destroyed, or the effect of the increased compactness of the medium is greater than the effect of whatever structure remains or any new structure which may have formed. Whichever the case may be, it is apparent that as the pressure is increased in this region a stabilized arrangement is forming and diffusion of the molecules is taking place more and more through the interstices which are not rapidly decreasing in size with pressure.

The irregularity in the 1 *N* Na₂SO₄ solution in the high pressure range may be due to ionic interaction at the higher concentration or to an additional desolvation effect not present at the lower concentrations.

25°C ISOTHERMS

The plots for the diffusion coefficient, activation volume ratio, activation enthalpy, and activation entropy⁶ for the sulfate solutions and water and sulfuric acid are shown in Figs. 12, 13, 14, and 15, respectively. The activation volume ratio is obtained for each iso-

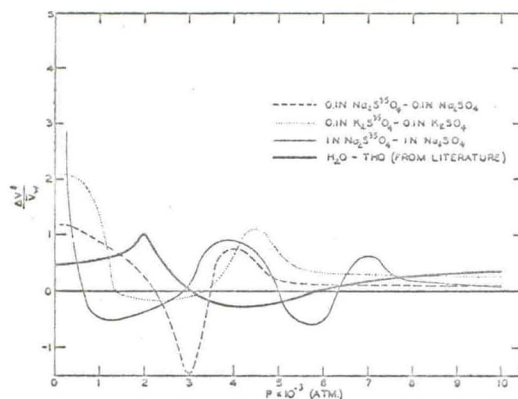


FIG. 11. Activation volume ratios for sulfate solutions at 50°C.

⁶ This term will be used in place of $\Delta S_p^\ddagger - \Delta S_0^\ddagger$.