

Fig. 12. Diffusion coefficients versus pressure sulfate solutions at 25°C.

therm independently, while the activation enthalpy and entropy depend on the displacement between two or more isotherms. Inasmuch as the structure of the solution varies widely with temperature, the activation enthalpy and entropy calculated probably do not apply to any one isotherm.

The similarity between water, 0.1 *N* H<sub>2</sub>SO<sub>4</sub> and 0.1 *N* Na<sub>2</sub>SO<sub>4</sub> are evident from Figs. 12 and 13, but the 1*N* Na<sub>2</sub>SO<sub>4</sub> and 0.1 *N* K<sub>2</sub>SO<sub>4</sub> have additional maxima and minima which are not easily explainable but which are definitely present.

In the low pressure region the increase in *D* and the negative activation volume indicate that the tetrahedral structure collapses locally during molecular motion. At pressures beyond the point where the collapse of structure dominates the motion of molecules, the water and sulfuric acid display a high degree of regularity associated with normal liquids. However, in this region the sulfate curves show irregularities, i.e., additional maxima and minima, which probably could be explained on the basis of the pressure dependency of desolvation and ionic interaction.

In the high pressure region Figs. 11 and 13 show that the activation volume ratios for all the solutions asymptotically approach approximately the same relatively low value, indicating a similarly stable structure for all solutions at very high pressure at both 25° and 30°C.

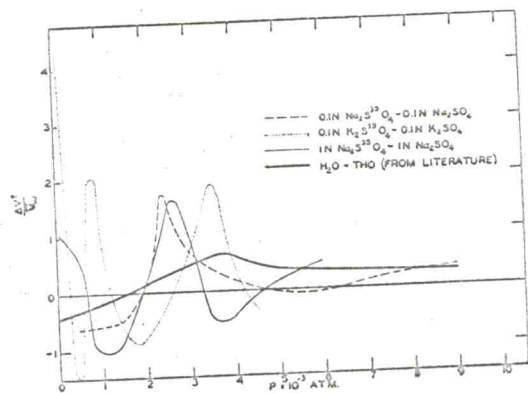


Fig. 13. Activation volume ratios for sulfate solutions at 25°C.

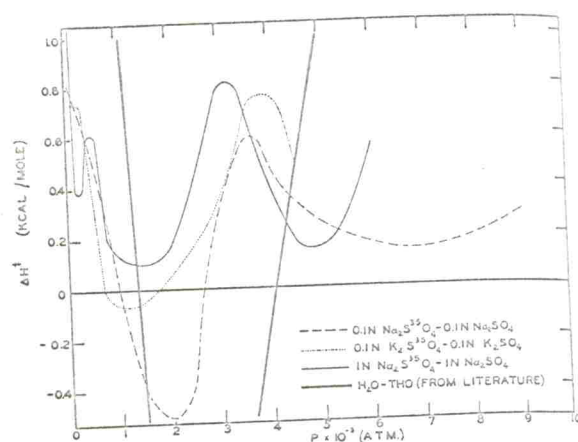


Fig. 14. Activation enthalpies for sulfate solutions at 37.5°C.

### 0°C ISOTHERMS

Figures 16 and 17 are plots of diffusion coefficients and activation volume ratios, respectively, versus pressure for the sulfate solutions and water and sulfuric acid.

There is a definite similarity between these sulfate curves and the water curve, and the similarity is even clearer between the sulfuric acid and 0.1 *N* sodium sulfate and among the water, 0.1 *N* potassium sulfate, and 1 *N* sodium sulfate.

In the very low pressure range, it appears that molecular motion is influenced by the more rigid structure that exists at 0°C. With the exception of the increase of *D* with pressure for the 1 *N* sodium sulfate and 0.1 *N* potassium sulfate in the initial pressure range, the curves all show the value of *D* decreasing to a minimum, rising to a maximum and dropping off in the high pressure range.

Molecular motion in the region where *D* initially decreases is controlled by the decrease in free volume, and the rigid structure at 0°C remains so and does not undergo any pronounced rearrangement with the initial application of pressure. Beyond the pressure where *D* is maximum, there is a general decrease in the value of *D* and an asymptotic leveling of the activation volume

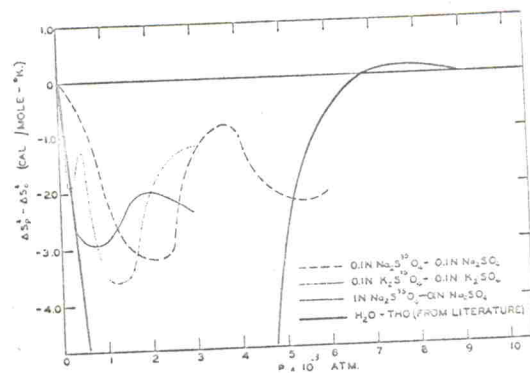


Fig. 15. Activation entropies for sulfate solutions at 25°C.

Fig. 16.

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