

Fig. 6. Activation volumes as a function of pressure. System: 0.1 N H_2SO_4 -0.1 N $\text{H}_2\text{S}^6\text{O}_4$.

the negative ΔV^\ddagger indicates that diffusion takes place almost entirely by localized collapse of the tetrahedral structure. Compressing beyond 900 atmos the activation volume increases indicating a positive local expansion in the activation process which is felt through an increasingly larger portion of the liquid as the free volume is decreased. At 3000 atmos ΔV^\ddagger has become virtually constant and increases only slightly with pressure to about 37 percent of the molal volume at 9000 atmos. The steady decrease of D and the very gradual increase of $\Delta V^\ddagger/\bar{V}$ beyond 3000 atmos indicate that the average configuration in the liquid must be stable with pressure.

At 50°C the situation is qualitatively similar to water at 50°. At first the diffusion coefficient decreases with pressure indicating a normal activation process relatively unaffected by the tetrahedral structure. At 3500 atmospheres the diffusion coefficient increases with pressure, passes through a maximum, and decreases in a normal manner.

The 0 and 5° isotherms of D are quite erratic and much like water at 0°. The influence of whatever structure may exist at atmospheric pressure is rapidly increased with the initial compression. This is shown by the rapid decline of D from about 1.0×10^{-5} at 1 atmos to about 0.27×10^{-5} at 335 atmos and 0°C. The sub-

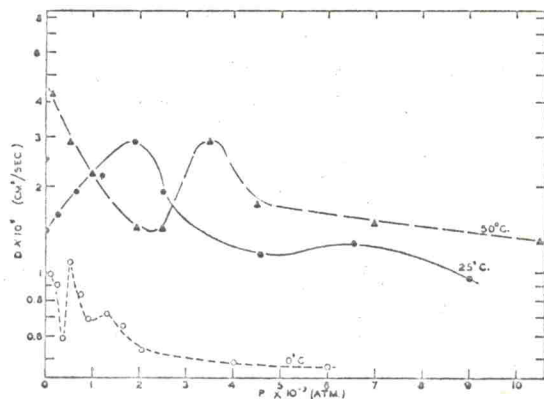


Fig. 7. Diffusion coefficients versus pressure 0.1 N Na_2SO_4 .

sequent ascent to a maximum of 0.95×10^{-5} at 840 atmos is equally rapid. Beyond 840 atmos D decreases and then settles to a plateau at 2000; at 3000 atmos it begins to decrease fairly rapidly again. In the range from 335 to 840 atmos the restricting configuration is apparently being broken down and D increases. At the 840 atmos maximum in D the tetrahedral structure no longer exists to a controlling extent, and we find the diffusion coefficient decreasing with pressure. The variation of the activation volume with pressure (Fig. 6) is consistent with our previous analysis.

It is seen in Fig. 5 that the 5° isotherm is similar to that for 0° as far as it was obtained (up to 1000 atmos).

The data for the three sulfate systems are shown in Tables III-V and Figs. 7-9. At first glance the results seem quite irregular, but the data were reproducible and very regular results were obtained for organic solutions on identical equipment. Extreme care was taken in nearly all cases to establish maximum and minimum points for the curves of diffusion coefficient versus

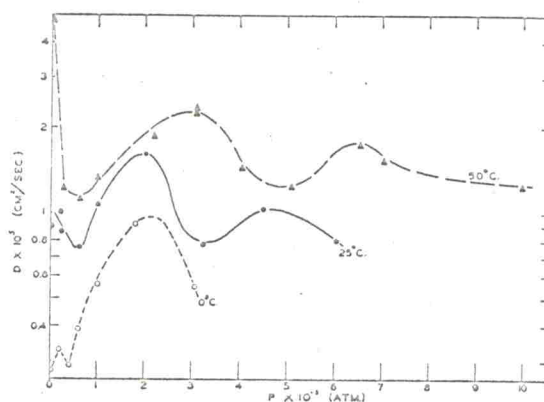


Fig. 8. Diffusion coefficients versus pressure in Na_2SO_4 .

pressure. This was accomplished either by making duplicate runs, or by making runs at small increments of pressure near what appeared to be a peak or dip in the curve. These check runs were found to reproduce the data within a maximum deviation of 10 percent.

Closer inspection of the original data do show very definite regularities, and these can be compared best by plotting the data of several isotherms together (Figs. 10-17) and are discussed in detail below. From these curves definite general conclusions can be obtained which are briefly stated at the end of the following paper.

50°C ISOTHERMS

A plot of diffusion coefficient versus pressure for the sulfate solutions and the water and sulfuric acid data³ at 50°C is shown in Fig. 10. The similarities to the water curve are evident. It appears that in all but a small pressure range (2250-4250 atmospheres) the process of diffusion in water is faster and that the motion of molecules is governed by effects which may be regarded

as superimposed on the case of water. logically be divided from atmospheric pressure to the first point to the high

The minimum value for 1 N sodium sulfate and potassium sulfate and sulfate. This decrease in pressure is normal in this range involves of the surrounding evident from the curves in this low activation volume $\Delta V^\ddagger/\bar{V}_w$, (see Fig. is greater than for sulfate solutions t

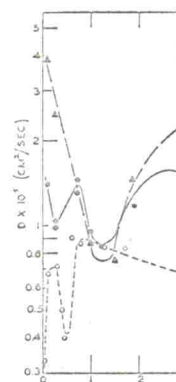


Fig. 9. Diffusion

largest for 1 N sodium sulfate and 0

As the pressure increases and passes as the solution is essentially by local co

The activation function of the atomic values for 0.1 N potassium for 0.1 N and 1 N ever, there is the of the activation exists which may responding atomic v

In the second activation volume largely due to the

In the pressure for D , the value of while the activation zero for a short ra

³ Hereafter this will