Fig. 2. Diffusion coefficient *versus* pressure high molecular weight 1 percent in toluene 25° and 50° isotherms.
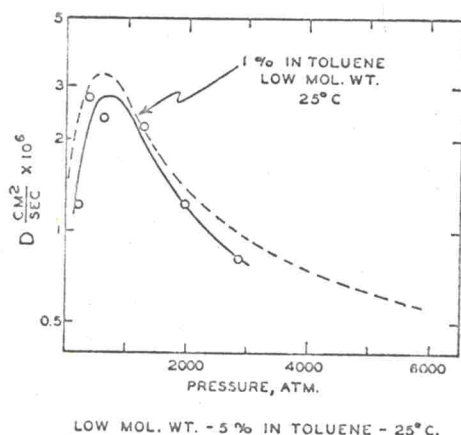

Fig. 3. Diffusion coefficient *versus* pressure low molecular weight 5 percent in toluene 25° isotherms.
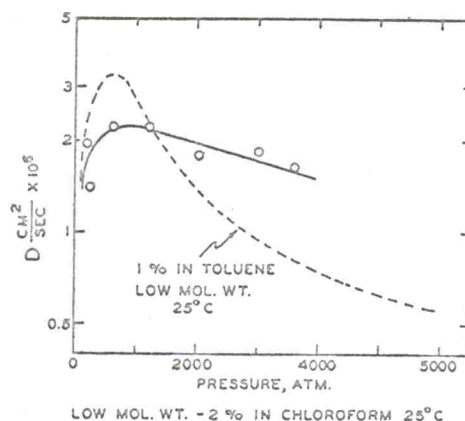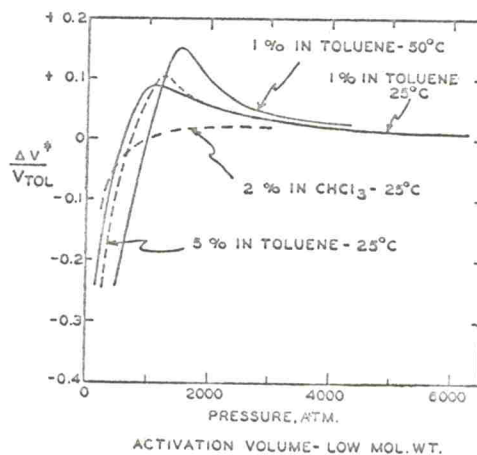
of a polymer molecule as loosely coiled in solution with large numbers of solvent molecules trapped in the coils. If a solvent molecule were expelled from one part of the coil, with or without trapping another solvent molecule in a different part of the coil, this would constitute molecular motion which might easily be characterized by a negative activation volume. Further, this mode of motion would become more difficult with increasing pressure, as the solvent molecules become squeezed out and the solvent structure more rigid. It is reasonable to believe that the segmental motion is controlling at the higher pressure.

The high molecular weight isotherm at 50°C is more difficult to explain. If the other curves are the result of two competing modes of motion it would seem that there are at least three competing modes in this case. The indicated reproducibility of the results shows that the shape of the curve is definitely radically different from the others. If the portions of the curve below 400 atmospheres and above 4500 atmospheres are extended to meet, the resulting curve is qualitatively similar to the other curves obtained. It is then the premature drop, at 500 atmospheres, which makes diffusion at

Fig. 4. Diffusion coefficient *versus* pressure low molecular weight 2 percent in chloroform.

curve although chloroform is a considerably better solvent for this polymer. The chloroform solutions proved to be very difficult to handle, which made further work along these lines impractical.

Evidently there are two mechanisms of molecular motion, one controlling at low pressure, and the second at high pressure.

The two mechanisms described below are consistent with our results and with other evidence of structure of polymers in solution, although they are certainly not the only possible descriptions of our results.

One possible mode of motion is segmental. This would result in a positive activation volume, and would therefore describe the controlling mechanism of motion in the high pressure region. The decrease in activation volume (per molal volume of solvent) and of activation enthalpy with pressure in this region would indicate a decrease in the size of the moving segment with pressure.

The second mode of motion depends on the picture

Fig. 5. $\Delta V^{\ddagger}/V_s$ *versus* pressure—low molecular weight polymer.