

$\text{Na}_2\text{SO}_4$  solution. It was found possible to duplicate almost exactly the curve previously obtained at  $25^\circ$  to 5000 atmospheres.<sup>3</sup> Although the two parts of cell were no longer the same length, one of the methods of calculation used previously<sup>1,10</sup> still applied. Very numerous preliminary runs indicated a reproducibility at least within 10 percent.

In each case the lower part of the cell (filter paper) was filled with a solution of nonradioactive polymer, and the upper sleeve was filled with radioactive polymer solution of the same concentration and molecular weight.

### RESULTS

The results are listed in Tables I-III and are plotted in Figs. 1-4. Figures 5-7 show the calculated quantities

TABLE I. Low molecular weight polymer.

Temperature °C	1% in toluene Pressure atmos	Diffusion coefficient $D$ $\text{cm}^2/\text{sec} \times 10^6$
25	80	1.59
25	200	2.36
25	360	2.18
25	360	2.99
25	640	3.24
25	970	2.63
25	1180	2.55
25	1600	1.83
25	1970	1.37
25	2000	1.24
25	3500	0.64
25	3500	0.83
25	3850	0.91
25	6000	0.68
25	6400	0.47
50	250	2.15
50	600	4.0
50	1050	6.8
50	1470	5.9
50	1870	3.29
50	3600	1.57
50	4550	1.20

TABLE II. High molecular weight polymer.

Temperature °C	1% in toluene Pressure atmos	Diffusion coefficient $D$ $\text{cm}^2/\text{sec} \times 10^6$
25	200	0.276
25	370	0.75
25	610	1.74
25	1220	1.50
25	1970	0.88
25	3650	0.45
50	200	0.73
50	350	1.24
50	600	1.19
50	1200	0.73
50	2000	0.71
50	2000	0.82
50	3500	1.12
50	3600	1.20
50	4500	1.21
50	4500	1.43
50	5650	0.45

<sup>10</sup> K. D. Timmerhaus and H. G. Drickamer, J. Chem. Phys. 19, 1242 (1951).

TABLE III. Low molecular weight polymer.

Temperature °C	5% in toluene Pressure atmos	Diffusion coefficient $\text{cm}^2/\text{sec} \times 10^6$
25	220	1.22
25	400	2.71
25	630	2.34
25	1280	2.16
25	1980	1.23
25	2850	0.80

Low molecular weight polymer 2% in chloroform

25	190	1.94
25	220	1.39
25	600	2.20
25	1200	2.22
25	2020	1.79
25	3000	1.84
25	3600	1.65

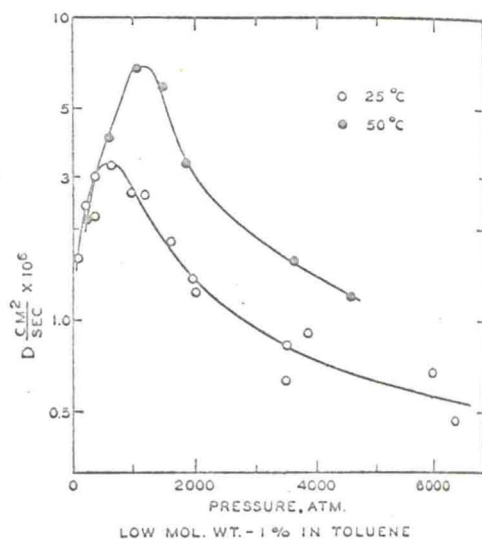


FIG. 1. Diffusion coefficient *versus* pressure low molecular weight 1 percent in toluene  $25^\circ$  and  $50^\circ$  isotherms.

(activation volumes, enthalpies, entropies, and free energies) for 1 percent toluene solutions of both molecular weights. Figure 7 shows activation volumes for the 5 percent toluene solution and 2 percent chloroform solution (both low molecular weight).

All the diffusion curves *versus* pressure (except the  $50^\circ$  isotherm for high molecular weight) show qualitatively the same features. In each case there is a rapid rise in  $D$  with pressure to 500 or 1000 atmospheres, followed by a slower decrease with increasing pressure. The low pressure part of the curve corresponds to a large negative activation volume in the low pressure region, and above 1000 atmospheres a positive activation volume decreasing with further increase in pressure.

Figure 3 indicates that there is only a minor effect of increasing the concentration from 1 percent to 5 percent by weight. The chloroform isotherm (Fig. 4) is qualitatively similar in shape to the corresponding toluene