

FIG. 6.  $\Delta V^\ddagger/V_T$  versus pressure—high molecular weight versus pressure.

50°C slower than at 25°C in the region (500–2000 atmospheres) which is to be explained, rather than the rise beginning at 1500 atmospheres.

It is possible that the molecular weight distribution of the high molecular weight polymer is bimodal, and that the "average" rate of diffusion is controlled by different molecular weights at different pressures. Unfortunately, because of the microsynthesis methods used, not enough of a cut was made to determine molecular weight distribution, but the fractionation was not sharp. Various other possible explanations can be put forward, but they are not particularly convincing. The high molecular weight polymer may be coiled in such manner at high temperature and low pressure that expulsion of solvent is not a particularly easy mode of

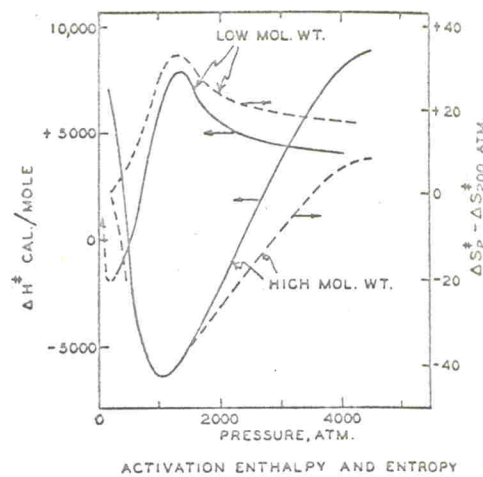


FIG. 7. Enthalpy and entropy of activation.

motion. The increase of pressure may increase coiling and increase the likelihood of this mechanism.

Light scattering experiments over this range of pressure are planned for the near future. It is hoped these will throw some light on the structure of polymer molecules in these solutions.

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