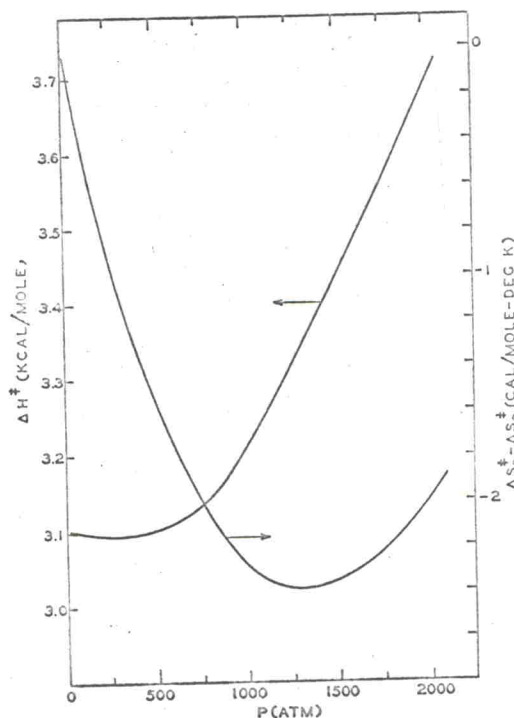
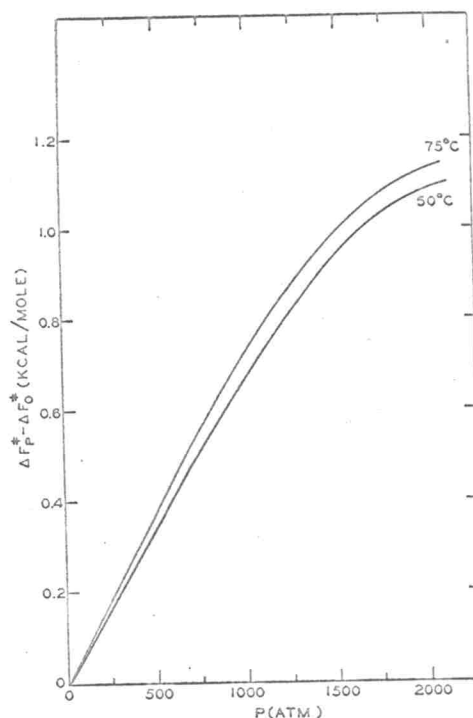
FIG. 2. $\Delta V^\ddagger/V$ versus pressure— CCl_4 — SnI_4 .

low value of ΔH_p^\ddagger shows that the enthalpy of the activated state does not increase relative to that of the normal state. Or, in other words, little energy is expended in accomplishing this volume increase. While

FIG. 3. ΔH^\ddagger versus pressure— CCl_4 — SnI_4 . $\Delta S^\ddagger - \Delta S_0^\ddagger$ versus pressure— CCl_4 — SnI_4 .

both $\Delta V^\ddagger/\bar{V}$ and ΔH_p^\ddagger are changed little, however, ΔS^\ddagger decreases considerably. The reason is found in the $\Delta S_p^\ddagger - \Delta S_0^\ddagger$ curve, which falls rapidly over this region. This means that the entropy of the normal state does not decrease as rapidly as does that of the activated state; that is, the number of degrees of freedom of the activated state are reduced relative to the normal state. Thus the increasing resistance to diffusion over the region below 1000 atmos is apparently caused by the requirement that as pressure increases the SnI_4 molecules must be more stringently oriented in the activated state. This conclusion becomes plausible if we consider the SnI_4 molecules as tetrahedra moving through spheres, or rotating CCl_4 molecules. It is obvious that

FIG. 4. $\Delta F^\ddagger - \Delta F_0^\ddagger$ versus pressure— CCl_4 — SnI_4 .

in order to diffuse through a medium of closely packed spheres a tetrahedral molecule can move with less distortion of the spheres, on the average, if it is oriented than if it moves without any orientation.

Above 1000 atmos the $\Delta V^\ddagger/\bar{V}$ drops sharply, showing that the amount of distortion needed to move is decreasing. The sudden rise in ΔH_p^\ddagger , however, shows that the energy expended to accomplish this smaller distortion is much greater than at lower pressures. The curve of $\Delta S_p^\ddagger - \Delta S_0^\ddagger$ levels and begins to rise, indicating that the degree of order imposed upon the normal state increases faster than that required of the activated state. The sharp decline in $\Delta V^\ddagger/\bar{V}$ with increasing pressure shows that diffusion is taking place more and more through existing holes, and accordingly indicates