

solute molecules. To test this possibility, we determined the dipole moment of 1,2-dichloroethane in decalin at 30° and atmospheric pressure to be  $\mu_0 = 1.42$  D. Under these conditions the dielectric constant of the decalin is 2.165, almost the same as that of *n*-hexane at 4 kbar. Consequently, while solvent changes due to pressure may have a small effect, we believe that the major part of the increase in dipole moment of dichloroethane is due to a pressure-induced distortion of the molecule which favors the *gauche* conformation.

To summarize this aspect of the work, we can say that the effect of pressure on the dipole moment is probably small for most molecules for  $P < 4$  kbar, and for alcohols it is likely to be negligible compared to the observed variation of  $\partial(\mu_0^2 g)/\partial P$ . Bridgman's compressibility experiments<sup>11</sup> show that  $(\partial E/\partial V)_T > 0$  for most liquids for  $P < 7$  kbar but upon further compression  $(\partial E/\partial V)_T$  changes sign. Presumably, for  $P > 7$  kbar the molecules themselves are being distorted and we anticipate that  $\partial\mu_0/\partial P$  will become significant in this pressure range.

We must then explain the observed decrease in  $g\mu_0^2$  at low temperatures and moderate pressures as being due to a change in the correlation factor opposite in direction to that due to intermolecular chain formation. Gilchrist's<sup>9</sup> suggestion regarding a more efficient packing at high pressure seems to us a reasonable one. Beginning with Kirkwood,<sup>4,14</sup> all attempts to evaluate the correlation factor of alcohols have focused attention on the correlation between a reference dipole and its neighbors in the same chain, the implicit assumption being made that the rapid breaking and reforming of hydrogen bonds will cancel out possible correlations between molecules in adjacent chains. In crystalline alcohol the parallel intrachain alignment must be cancelled by an antiparallel interchain alignment in order that there be no net electric polarization. As the pressure on the liquid is increased, chainwise association is favored and undoubtedly the average packing approaches that of the solid. We suggest that the onset of this rather extensive short-range order is reflected in the decrease of the correlation factor with pressure.

## Thermal Diffusion in the Nonpolar-Polar System Helium-Methyl Chloride

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The thermal diffusion factor  $\alpha_T$  for a 1:1 mixture of He and  $\text{CH}_3\text{Cl}$  has been measured by the two-bulb method at different temperatures ranging from 338°–530°K. The composition dependence of  $\alpha_T$  for this system has also been studied at 362.8°K. For the temperature dependence of  $\alpha_T$  the agreement between experimental and calculated values is poor even when inelastic collisions are taken into account. For the composition dependence of  $\alpha_T$  the theoretical and experimental curves run approximately parallel to each other over the whole composition range. This probably means that the inelastic collisions do not play a significant role in the thermal diffusion phenomenon of this system.

### I. INTRODUCTION

The calculated values of the transport properties of nonpolar gases have been found to have better accord with the experimental observations than those for the polar gases. This is mainly due to the long-range angle-dependent part of the intermolecular potential between two polar molecules which also makes the probability of inelastic collisions high. The intermolecular potential for polar molecules is generally represented by the Stockmayer or 12-6-3 potential<sup>1</sup> which contains the angle-dependent dipole-dipole interaction term varying as  $r^{-3}$ . However, in evaluating the collision integrals required for the calculation of the transport properties

approximations are made so that effectively a spherically symmetric potential is used.

Monchick and Mason<sup>2</sup> have calculated the collision integrals for the 12-6-3 potential by assuming that the relative orientation of the dipoles does not change during a collision and that all relative orientations are equally probable. For most molecules at ordinary temperatures the rotational energy is much less than the translational energy which is of the order of  $kT$ . Consequently, when this condition is valid inelastic collisions should have little effect on the trajectories of the colliding molecules. This approximation should hold reasonably well for transport properties like diffusion and viscosity which to the first approximation are not affected by

<sup>1</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), hereafter referred to as MTGL.

<sup>2</sup> L. Monchick and E. A. Mason, *J. Chem. Phys.* **35**, 1676 (1961).

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