

bution due to internal energy was calculated by the relation

$$k_{ie}(X, P) = \chi_1 F_1 P_1(1 \text{ atm}) D_{11}(1 \text{ atm}) \left[C_{V_1}(P) - \frac{3}{2} \frac{k_B}{m_1} \right] + \chi_2 F_2 P_2(1 \text{ atm}) D_{22}(1 \text{ atm}) \left[C_{V_2}(P) - \frac{3}{2} \frac{k_B}{m_2} \right] \quad (8)$$

The results of the calculation were very disappointing, with deviations from the experimental values of as much as +75%. Selected individual results are given in Table II, along with values of k_{ie} . The deviations were much larger than those obtained for the pure gases, and were, in almost every case, positive deviations which were larger than the calculated contribution of the internal energy. This seems to indicate that the Enskog mixture equations, when applied in this manner, are not good approximations to the physical situation. This is probably due to the fact that they do not include the effects of attractive forces between molecules.

The Cluster Theory

It is well known that gases at low temperatures form clusters (8, 19) of two or more molecules. These clusters can be considered as short-lived compounds which have finite heats of reaction. The equilibrium concentrations are functions of temperature, and if the relaxation time is short, equilibrium will be approached at every point in a gas through which heat is being transferred. If the reaction between two monomers to form a dimer is exothermic, the equilibrium concentration of