

to the molecular diameter itself. Various corrections for this effect yield positive results only for moderately dense gaseous mixtures. With further increase in pressure (in particular at temperatures not much above the critical), the corrections become unsatisfactory due to the absence of a correct equation of state.

The following is an example for such a deviation. In 1956, the English workers R. Lard, A. Morrel and L. Sid published a paper in the issue of the Discussions of the Faraday Society devoted to the physico-chemical processes at high pressures on the kinetics of thermal polymerization of ethylene at 200-360° at 1200-2000 atm. According to the proposed reaction mechanism the polymerization rate should have been proportional to the squared concentration of ethylene. The empirical kinetic equation gave completely unexpected results: the exponent of the ethylene concentration was ten times greater (about 20). This discrepancy was attributed to the varying rate constant with increasing pressure.

The effect of pressure on rate constants is of special interest in this field. To analyze this effect the structure and properties of the activated complex must be known. In distinction to the activated collision theory, the theory of transition state considers the interaction of two or more particles, not as an instantaneous act, but as a lasting process with accompanying energy change in the system. The state of the system in which the potential energy equals the peak of the reaction energy barrier is called transition state or activated complex. A better knowledge of the transition state is of enormous importance for chemistry, since the structure and properties of the activated complex determines the mechanism of the elementary act in a chemical process.

Pressure has a considerable effect on liquid phase rate constants.