

Menshutkin reaction is a convenient example since the activated complex model is known usually with sufficient accuracy to estimate Δv^\ddagger for the overlapping sphere of the van der Waals radii. This work and the subsequent experimental investigations, performed by the author and B. S. Elyanov in the Institute of Organic Chemistry, have confirmed in full the above hypotheses and allowed the introduction of the supposition that in some reactions the volume contraction during activated complex formation is a measure of steric hindrance.

An interesting application of high pressure is in the field of collective interactions such as polymerization. Let us assume that the activated complex contains a large number of molecules, n . In that case Δv^\ddagger is roughly $(n-1)$ times larger than in a bimolecular reaction. A polymorphic transition may serve as an example. R. Ventorf reported in the XVII International Congress on Pure and Applied Chemistry on the effect of pressure on the reaction rate of the polymorphic transition of diamond into graphite at 1700-2200°. Pressure retards the reaction significantly (the experiments were performed in a vacuum and at 20,000 atm). Ventorf estimated $\Delta v^\ddagger \approx 168 \text{ cm}^3/\text{gr atom}$, which is 50 times more than the volume occupied by 1 gr atom of carbon in crystalline form. It was concluded that the polymorphic transition of diamond to graphite is a collective act in which a large number of carbon atoms participate.

The mentioned polymorphic transition is characterized by volume expansion during transition state formation (Δv^\ddagger positive). For Δv^\ddagger negative the reaction rate is expected to increase with increasing pressure, such as in polymerizations. Pressure effect studies may indicate the fact of collective interaction and also give some information on the number of participants in this interaction.