where b_1 is the constant of the van der Waals equation, which is equal to four times the volume of the molecule. It is easy to see that equation (II) leads to the conclusions that the velocity constant increases with an increase in the pressure. This is confirmed in particular by experimental data on the thermal decomposition of hydrogen iodide under pressure.[11] The velocity constant for first-order gaseous reactions should, it appears, decrease slightly at high pressures (see 3)).

Nevertheless the effect of pressure on the velocity of most reactions in real gases is to a large extent governed by the change in concentration of the reactants. Thus, in the previously mentioned investigation of the decomposition of HI it was found that in the pressure range investigated (approximately up to 250 atm.) the velocity of the reaction increased 39.6 times (increase of the original concentration of HI by a factor of 21.9 and an increase of the velocity constant by a factor of 1.8).

For liquid-phase reactions, on the other hand, the change in the concentration of the reactants caused by the increase in pressure is comparatively small, owing to the much smaller compressibility of liquids in comparison with gases. Here the decisive factor is the pressure-dependence of the velocity constant for the reaction. In so-called normal reactions in the liquid phase, an increase in pressure up to 3000 atm. causes the velocity constant to increase by a factor of 1.5 to 2, and up to 5000 atm. by a factor of 2-3. The velocity constants of "slow" reactions increase considerably more rapidly with an increase in the pressure, often by a factor of 10-15 or more when the pressure is increased to 5000 atm. Decomposition reactions in the liquid phase are often retarded by an increase in the pressure (see 12)).

It may be noted that the pressure-dependence of the velocity constant of a reaction in the liquid phase is satisfactorily explained and also (in the simplest case of addition reactions) quantitatively interpreted by the transition state theory (see 13), 3)).

Application of the theory of transitional states leads to the equation:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT} , \tag{III}$$

where $\Delta V^{\neq}$ is the change in volume associated with the formation of the activated complex (per mole).

In reactions between two or more substances the molar volume of the activated complex is, as a rule, smaller than the sum of the molar volumes of the reactants, since the separation distance between the molecules (atoms) composing the activated complex only slightly exceeds the normal length of chemical bonds. Therefore, according to equation (III), the velocity constant of such reactions should as a rule increase with the pressure.

For unimolecular decomposition reactions the bond undergoing rupture in the activated state is stretched; consequently, the molar volume of the substance in its activated state is rather larger than in its usual state. The velocity constant of such reactions, according to equation (III), should decrease slightly as the pressure is increased.

The effect of pressure on the velocity of a reaction can lead to considerable changes in the composition of the products of a complex process, i.e. on the course of the reaction. As an example may be cited the copolymerisation of ethylene and carbon monoxide in cyclohexane.[14] On increasing the pressure from 1.6 to 306 atmosphere, not only was the molecular weight of the polymer increased (from 280 to 3400), but also the proportion of combined CO in the polymer became larger (from 12.6 to 41.8%), i.e. the chemical composition of the polymer was altered. The production of the highly polymerised polyethylene (polythene) in the presence of a very small amount of oxygen at pressures of more than 1000 atm.[15] is apparently likewise dependent on such a marked acceleration of the chain-polymerisation of ethylene as a result of the application of high pressure.