In parallel reactions the equilibrium is of course displaced towards the products whose formation is completed with the greatest decrease of volume.

The effect of pressure on chemical equilibrium may lead to a substantial change in the composition of the products, i.e. in the course of the reaction. We will give some examples. In multistage polymerisation, high pressure shifts the equilibrium towards products with a higher molecular weight [4]. The reversible polymerisation of butyraldehyde and isobutyraldehyde under pressure is described in the literature.[5], [6] The polymers, obtained at pressures of up to 12,000 atm., slowly depolymerised at atmospheric pressure to give the original aldehydes. It appears that in this case polymerisation and depolymerisation are mainly associated with the effect of high pressures on the chemical equilibrium.

It is further known that many metal carbonyls are stable at their formation temperature only under conditions of high pressure (e.g. $Co(CO)_4$). Another example is the action of carbon monoxide on cobalt iodide at room temperature under pressure to give the unstable compound $CoI_2.CO$, which decomposes at atmospheric pressure.[7]

Because high pressure guarantees the stability of a series of unstable compounds, it has a marked effect on the course of certain catalytic reactions. For example, in the Oxo synthesis (the synthesis of alcohols from olefines, hydrogen and carbon monoxide over a cobalt-containing catalyst), the catalyst is probably not the cobalt itself, but a carbonyl or hydrocarbonyl of cobalt, which is only stable at high pressure. It is very characteristic that at atmospheric pressure the hydrocondensation of olefines with carbon monoxide and hydrogen produces not oxygen-containing compounds, but mainly hydrocarbons.[8], [9] A similar pressure-dependence of the composition of the products is found in syntheses starting from carbon monoxide and water.[10]

Many other examples of the effect of high pressure on the course of reactions by shifting the position of equilibrium could be given.

We will now examine the question of the influence of high pressure on the velocity of chemical reactions. It has already been mentioned above that in a mixture of ideal gases the concentrations of the components are proportional to the pressure; this also determines the pressure-dependence of the velocity of gaseous reactions when the pressure is small and the temperature is sufficiently high. In such cases the velocity constant itself does not depend on the pressure.

In real gaseous systems the dimensions of the molecules cannot be neglected in comparison with the lengths of their mean free paths. An approximate treatment of this case on the lines of the theory of active collisions for second order reactions leads to the conclusion that the velocity constant increases with the pressure.

It will be remembered that according to the theory of active collisions the number of two-component collisions leading to reaction is equal to $z_0 e^{-E/RT}$. Here,

$$z_0 = n_1 n_2 (r_1 + r_2)^2 \sqrt{\frac{8 \pi RT(M_1 + M_2)}{M_1 M_2}} , \qquad (I)$$

where n_1 and n_2 are the numbers of molecules of gases 1 and 2 in 1 cc; r_1 and r_2 are the radii of these molecules; M_1 and M_2 are their molecular weights; and E is the energy of activation. When $n_1 = n_2 = 1$, the number of active collisions is the velocity constant for the reaction, k.

When the pressure is increased, appropriate corrections must be introduced into equation (I). Thus, for example, according to the van der Waals correction, the number of binary collisions in the moderately compressed gas, z_0' is given by the equation:

$$z_0' = z_0 \cdot \frac{1}{1 - \Sigma n_i b_i} , \qquad (II)$$