

Application of high pressures to the investigation of the
mechanism of chemical reactions

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Nature and basis of the method

Investigations of the mechanism of chemical reactions vary widely in their approach to the solution of a particular problem. Some of them aim at comparing the relations between certain atoms or groups of atoms before and after reaction. They include many investigations using labelled atoms. The aim of other investigations is the study of the effect of different variables in a chemical reaction on the course of the reaction; the observed changes can be compared with expectations on the basis of this or that scheme of reaction mechanism. Belonging to this group of investigations, in particular, are kinetic studies, which we will discuss in rather more detail.

Among the variables of a chemical process are the concentration of the components, the temperature, the pressure (or volume) and the duration of the process. The study of the effect of changes in concentration of the reactants on the velocity of the process is the standard kinetic method for investigating the mechanism of reactions. The change in the velocity of the process with temperature allows one to determine the value of the energy of activation (often called the "apparent" energy of activation) which in a series of cases indicates the character of the rate-determining step of the overall process.

Changes of pressure in gas-phase reactions are normally considered as equivalent to changes in concentration. This, however, is only true (and that approximately) for mixtures of gases at low pressures, and at temperatures considerably greater than the critical temperatures of the given gases; in other words, the concentration is proportional to the overall pressure only in the case of ideal gases. High pressure is an important parameter, whose change has a specific influence not only on the velocity, but also on the course of chemical processes. This is especially clearly seen in the case of liquid-phase reactions where the influence of pressure is only linked to an insignificant degree with changes in concentration.

If we know the laws of the effect of high pressure on the course of reactions of various types, we can apply them to a study of the mechanism of chemical processes.

The high-pressure approach to investigation of the mechanism of a chemical reaction consists essentially in studying the effect of high pressure on the velocity and the course of the reaction, and comparing the resulting data with results expected on the basis of possible schemes for the mechanism of reaction.

At present an overwhelming majority of investigations of chemical reactions at high pressure are carried out in the region of up to 1000 atm. Only in a few cases have pressures up to 10-12,000 atm. been applied. The results of these investigations indicate that at pressures of a few hundreds or thousands of atmospheres, as a rule, fundamental changes in reactivity do not occur. This is primarily due to the absence of any significant deformation of the molecules (atoms), radicals and ions at these pressures. In fact, from examination of compressibility data one may infer that significant deformation of molecules (atoms) of most substances occurs only at pressures of the order of tens of thousands of atmospheres.