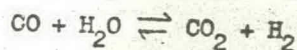


The ability of substances to take part in chemical reactions is known to depend also on the reaction medium, and, in particular on its electrical and other physico-chemical properties. If we wish to use high pressures for the study of the mechanism of chemical processes, it is desirable in most cases that the influence of the medium on the course of the process which is to be studied should not depend substantially on the pressure. It is found that the variation of most physico-chemical properties of liquids in the range of pressure up to a few thousand atmospheres is not generally very significant. Transport phenomena are an exception to this rule; for example, the viscosity of liquids increases rapidly with an increase in pressure. This is one of the reasons why an increase in pressure can transfer a reaction from the field of kinetics to that of diffusion. On the basis of the above-mentioned considerations and the available experimental data, it is generally advisable to use pressures up to 2,000-3,000 atm. to investigate the mechanism of chemical reactions.*

In the first place we must examine the question of the effect of high pressure on the velocity and the course of various chemical processes. We commence our discussion by considering the problem of chemical equilibrium.

For a mixture of ideal gases, the shift in chemical equilibrium with a change in pressure is determined by the change in the number of moles during the reaction on the basis of the stoichiometric equation for the reaction. If the reaction proceeds with a diminution in the number of moles, the equilibrium concentration of reaction products will increase with an increase in pressure, *vice versa*.

For a mixture of real gases, the relation between the chemical equilibrium and the pressure is more complicated and depends on the compressibility of the mixture at various pressures and compositions. Thus, for example, the water gas equilibrium



is shifted to the left by an increase in pressure, despite the fact that this reaction proceeds with no change in the number of molecules.

For reactions in the liquid phase, the influence of pressure on chemical equilibrium is less significant than for gaseous systems. However, in isolated cases it may prove to be quite marked. If, for example, the reaction $\text{A} + \text{B} + \dots \rightleftharpoons \text{P} + \text{Q} + \dots$ is accompanied by a decrease in volume ($-\Delta V$) of 25 cc/mole, the equilibrium constant

$$K_N = \frac{N_P \cdot N_Q \dots}{N_A \cdot N_B \dots}$$

at 100°C is increased 135 times when the pressure is increased from 1 to 6000 atm. Such large values of ΔV are frequently found in liquid-phase reactions, proceeding with a diminution in the number of moles. Thus, for the dimerisation of cyclopentadiene at 40°C the value of ΔV is -33.2 cc/mole at 1 atm., -31.1 cc/mole at 500 atm., and -27.6 cc/mole at 1000 atm.²⁾

In the solid phase, the change of volume during a reaction, which determines the pressure-dependence of chemical equilibrium, is usually even smaller than in liquids. Some exceptions to this rule are found in particular in decomposition reactions of solids, where not only solid but also gaseous products are formed, and are removed from the sphere of reaction.

We will not consider here the dependence of chemical equilibrium on pressure in gas - liquid, gas - solid and liquid - solid systems, nor in polyphasic systems (in this connection see 3)).

* For the investigation of some problems concerning the mechanism of reaction (e.g., steric hindrance) very much greater pressures should be used (see 1)).

** N = mole fraction.