

Brief Communications

Determination of the reaction acceleration effect at an elevated hydrostatic pressure

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A method was proposed for the calculation of changes in the rate ($k_p/k_{p=0}$) and equilibrium constants ($K_p/K_{p=0}$) for chemical reactions under high hydrostatic pressure (10–20 kbar). The calculation based on the activation and reaction volume data makes it possible to select optimum conditions for slow and equilibrium chemical processes.

Key words: high pressure influence, activation volumes, reaction volumes, calculation of acceleration effect.

The occurrence of chemical reactions depends on internal and external factors. The influence of high hydrostatic pressure can be attributed to external physical factors. Catalysis and elevated temperature substantially help slow irreversible reactions to occur, whereas slow equilibrium reactions can usually be carried out only under conditions of high hydrostatic pressure. An increase in the rate and equilibrium constants for processes occurring with a volume decrease are favorably combined only under high pressure conditions.^{1–6}

The dependences of the equilibrium (K)⁷ and rate (k)^{8,9} constants of the process on the external pressure (P) are described by the following equations:

$$\partial \ln K / \partial P = -\Delta V / (RT), \quad (1)$$

$$\partial \ln k / \partial P = -\Delta V^\ddagger / (RT), \quad (2)$$

where ΔV and ΔV^\ddagger are the reaction and activation volumes, respectively; and P is the excessive hydrostatic pressure. There are numerous examples for the successful occurrence of the reactions at an elevated (10–20 kbar) pressure only, whereas the occurrence of these reactions are often impossible under normal conditions.^{1–6} In the most cases, the experimental dependences of the rate or equilibrium constants on the pressure are determined in the range below 2–3 kbar, and these dependences are reliably described by the following polynomials:

$$\ln(k_p/k_{p=0}) = aP + bP^2, \quad (3)$$

$$\ln(K_p/K_{p=0}) = cP + dP^2. \quad (4)$$