If the experimental data satisfy equation (X), this indicates the usefulness of the above simplified scheme for the mechanism of polymerisation. In calculations according to this scheme, the effect of the walls and of impurities in the reaction mixture, and also of other factors (e.g. the change in the viscosity of the medium at high pressures), is eliminated by reducing the value of the velocity at a given pressure to that which it would have during the formation of a polymer of constant molecular weight at atmospheric pressure.

Equation (X) was tested on kinetic data for the thermal polymerisation of styrene under pressure 44) and on dilatometric data for the decrease in volume occurring during the polymerisation of styrene at various pressures 45). The results of the calculations are shown in Table 4.

Table 4

Block polymerisation of styrene at 100°C.

$$[k'_p] = k'_{o(p)} : k'_{o(1 \text{ atm.})}$$

p (atm.)	k_o % change/hr.	$k_p \times 10^{-5}$	$[k_p]$ Experimental	Calculated
1	3.40	4.40	1	1
1000	5.06	6.69	1.0	1.93
2000	15.09	7.10	2.93	3.25
3000	34.3	8.28	5.42	5.22
4000	50.0	9.18	7.13	8.16

As we can see from Table 4, the calculated and experimental values of $[k'_p]$ agree adequately at pressures of 2000, 3000 and 4000 atm.; only at a pressure of 1000 atm. is a significant divergence found. The assumptions on which the calculation is based therefore appear to be valid.

a) Isotopic Ion-Exchange Reactions

The investigation of the effect of pressure on the rate of isotopic exchange reactions is of interest, since these reactions are distinguished by complete equality of the molar volumes and the compressibilities of the reactants and the products. Hence, pressure has here no effect on the chemical equilibrium.

The exchange reaction between alkyl halides and alkali metal halides in alcoholic solution is an ion-molecule reaction, as shown by recent work: 46)

$$\overset{*}{Hal}^- + RHal \to R\overset{*}{Hal} + Hal^-.$$
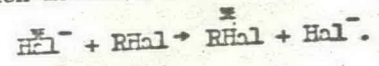
In this case it is to be expected that increased pressure will speed up the reaction, since in chemical reactions between two or more molecules the formation of an intermediate compound is usually associated with an increase in volume (see 3)).

Experiment confirms this hypothesis. A study 47) has been made of the effect of pressure on the rates of the isotopic exchange reactions between propyl iodide and I^{131} ions, and between propyl bromide and Br^{82} ions. It was shown that these reactions are accelerated by pressure like "normal" bimolecular reactions; thus, for example, the velocity constant of the former reaction increases more than $2\frac{1}{2}$ times as the pressure is increased from 1 to 2400 atm. Results of high pressure investigations of reactions have therefore so far confirmed facts obtained with the aid of other methods.