

function of Cr . When $Cr = 0$, the rate is proportional to the second power of the concentration of the acid; on addition of potassium bichromate the power diminishes until $Cr = 80$, when the rate is proportional to the first power of the concentration of the acid, and the curve (Fig. 2) becomes a straight line.

In Ostwald's "*Lehrbuch der Allgemeinen Chemie*" II (2), p 262, that author says: "So long as the catalyser is neither altered, formed, nor destroyed by the reagents or products of the reaction, its influence is exerted only on the value of the velocity constant, and not on the character of the kinetic equation." The present case is evidently an exception.

INTERPRETATION OF THE RESULTS

These results may be expressed by assuming that:

(i) In solutions containing bromate, bichromate acid and iodide, two reactions take place simultaneously, both resulting in the liberation of iodine.

(ii) The rate of the first reaction is proportional to the concentrations of the bromate, and iodide and to the square of that of the acid; while that of the second is proportional to the concentrations of bromate, iodide and acid, and slightly less than proportional to that of the bichromate.

(iii) The second reaction takes place without proportional reduction of the bichromate.

The corresponding kinetic differential equations are:

$$\frac{\partial x}{\partial t} = K_1(A-x)(B-x)(C-x)^2, \text{ and}$$

$$\frac{\partial x}{\partial t} = K_2(A-x)(B-x)(C-x)Cr$$

and the rate at which iodine is liberated in the solution:

$$\frac{dx}{dt} = (A-x)(B-x)(C-x)(K_1C-x + K_2Cr) \quad (4)$$

The values of the two constants in this equation were calculated from the two experiments of Table VI in which $Cr = 0$ and $Cr = 100$ respectively; they are, $K_1 = 645 \times 10^{-12}$ and $K_2 = 333 \times 10^{-10}$. The change of n with the concentration of the bichromate (Table VI and Fig. 2) is in quantitative accord with these assumptions, as may be seen by