

A REACTION WHOSE RATE IS DIMINISHED BY RAISING THE TEMPERATURE

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Towards the close of my measurements of the rates of the reactions in solutions containing chromic acid, potassium iodide and ferrous sulphate,¹ I was surprised to find that the amount of iodine liberated in a minute at 30° was less than that set free in the same time at 0° (see Table 21).

Taken by itself, this result does not prove that the rate of liberation of iodine is less at 30° than at 0°, and at first I thought it most likely that at the higher temperature the reaction was over before the minute was up. Analyses at the expiration of two, four and eight minutes, however, showed that, far from being completed within sixty seconds, the reaction was still proceeding after four minutes; and as in blank experiments (no FeSO_4) no iodine was set free inside of eight minutes, the conclusion is unavoidable that the oxidation of potassium iodide by chromic acid in presence of ferrous sulphate is retarded by raising the temperature.

The measurements detailed in the following tables show that the nature of the reaction at 30° is much the same as at 0°. At the higher temperature, as at the lower, the rate is proportional to the first power of the concentration of the iodide (Tables 21 and 25), to the first power of the concentration of the ferrous salt (Tables 24 and 26) and to the 1.7th power of the concentration of the bichromate (Tables 24 and 27). The retarding influence of the products of oxidation (Tables 21, 28, 31 and 30) is somewhat less at the higher temperature, and its "ageing" (Tables 15 and 26) is more rapid. In experiments carried out without addition of the products of oxidation, the rate is proportional to the fourth power of the concentration of the acid (Tables 31 and 32):

¹ Jour. Phys. Chem. 7, 356, 1903.