

while in their presence it varies with the second or third power only (Tables 24, 33 and 34). At zero, in the presence of excess of the products of oxidation the rate is proportional to the fourth power, while in the absence of ferric salts the reaction is too quick for accurate measurement. It is a consequence of this difference in the order of the reaction with respect to the acid, that while in Tables 24, 25, 26 and 27 the reaction is four or five times as quick at 0° as at 30.2°, in Tables 33 and 34 where large quantities of the acid were employed, it is seven and fifteen times as quick, respectively.

A single experiment (Table 35) shows that, as was to be expected, the rate of oxidation of ferrous sulphate by chromic acid in absence of potassium iodide is accelerated by heat; Mr. DeLaury¹ has found that the same is true for the oxidation of potassium iodide in absence of ferrous salts.

The only reactions hitherto studied whose rates have a negative temperature coefficient, so far as I am aware, are those in which a colloidal catalytic agent is involved; in these cases the rate passes through a maximum as the temperature is increased, and then falls off because of the coagulation of the colloid. In the experiments of the present paper the only colloid present is the ferric salt, and its coagulation instead of retarding, accelerates the reaction.

It seems probable, however, that as the rates in other complex systems came to be studied, further cases of negative temperature coefficients will be met with, and that the present instance may be regarded as typical of a new class. Both ferro-iodion theory and peroxide theory are ready with an explanation of the retardation; the former by assuming that the amount of FeI undissociated is less at high temperatures, and the latter by asserting that as the temperature is raised the peroxide reacts more with the residual ferrous salt, and less with the iodide.

I regret that in the time at my disposal I am not able to undertake the large amount of work necessary to ascertain whether either theory could be brought into accord with quan-

¹ Jour. Phys. Chem. 7, 230 (1903).