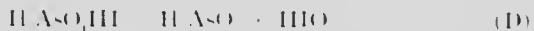


rates give K' , almost constant but when R_s is small they show an increase. It offers a satisfactory escape from the conclusion noted on page 732 of the lack of independence of the constituents. It supplies a good reason for the small values of K_s in Tables 2-13. The increased value in Table 1 may safely be attributed to the divergence of the sulphuric acid from the simple laws when in concentrated solution (4.8 normal). It must also be observed that in the direct rate measurements (Table 1, page 379, of former paper) the sulphuric acid increases its action faster than its concentration when 2.0 normal but its action is still proportional to its concentration when 0.93 normal.

Such a relation may be explained theoretically by the assumption of a reaction in two steps neither of which is instantaneous. This possibility has been discussed¹ theoretically in several papers but I am not aware of any practical application. The equilibrium of the first step is not quite attained while the reaction of the second step is removing one or more of the products of the first, or conversely. In this case some hints may be obtained as to the probable steps. First, no product of the reaction retards the reverse rate so that the first step must be one of addition or at least one that does not produce either of the products of the final reaction. Second, the rôle, normal and abnormal, of the potassium iodide and the sulphuric acid are very similar so that they probably play similar parts in both steps: this is confirmed when hydriodic acid is substituted for potassium iodide and sulphuric acid. Third, arsenic acid must enter the first step. The separation of a very small quantity of a crystalline compound during some of the fast reverse rate measurements, is in line with this hypothesis. Consequently a probable first step is



where water may be also split off. The second step could then be



To supply the desired explanation it is only necessary that the

¹ Bancroft, Jour. Phys. Chem., **4**, 75, 1900; Mittasch, Zeit. phys. Chem., **40**, 1, 1902; Jungius, Zeit. phys. Chem., **49**, 368, 1904.

² Quantity too small for analysis.