## [MILLER]

## IDEA IN CHEMICAL MECHANICS

aeids of the halogens, had been studied by Burchard<sup>2</sup> in the laboratory of Lothar Meyer, by Ostwald,<sup>5</sup> by Meyerhoffer,<sup>4</sup> by Dr. Schlundt<sup>5</sup> in Wiseonsin, by Warder,<sup>6</sup> of Washington, by Magnanini<sup>7</sup> in Italy, and by Pendlebmy and Seward,<sup>8</sup> and Judson and Walker<sup>9</sup> in England. Most hight had been thrown on the reaction by Prof. Noyes,<sup>10</sup> but in the opinion of the last chemists to work on this subject. Messrs. Judson and Walker, expressed in 1898 after a review of the earlier papers: "The action of hydriodic acid on the oxyacids of the halogens is of too intricate a nature to give any satisfactory numerical results."

Attacked by the method of systematic exploration, however, this problem proved easy of solution; Messrs. Bray,<sup>14</sup> Dushman <sup>12</sup> and Clark<sup>13</sup> expressed the relations between concentrations and rate in mathematical form, traced out the influence of the iodine liberated during the reaction, and recalculated most of the experimental work of their predecessors. The remarkable catalytic action of chromic acid on one of these reactions, discovered by Ostwald, has also been studied in detail.<sup>14</sup>

In this connection, it became apparent that reactions of the fourth order are plentiful as blackberries in August; and in the oxidation of ferrous salts by chromie acid, Miss Bensen<sup>15</sup> found one of the fifth. The opinion held between 1884 and 1895, that reactions of a higher order than the second are curios, must, therefore, be given up. It probably arose from the circumstance that the method of investigation employed was unable to cope with the complicated cases.

Some of these results might conceivably have been attained by a judicious use of method number three. It is otherwise with the reactions to which I will now refer.

Schwicker,<sup>16</sup> who studied the formation of iodate by the action of iodine on caustic potash in 1895, thought that he had discovered a re-

<sup>8</sup> Zeit, phys. Chem., 2, 796 (1888).
<sup>8</sup> Zeit, phys. Chem., 2, 127 (1888).
<sup>9</sup> Zeit, phys. Chem., 2, 585 (1888).
<sup>9</sup> Am. Chem. Jour. 17, 754 (1895).
<sup>8</sup> Am. Chem. Jour. 18, 23 (1896).
<sup>9</sup> Gazz. Chim. Ital., 21, 476 (1891).
<sup>9</sup> Proc. Roy. Soc., 45, 396 (1889).
<sup>9</sup> Jour. Chem. Soc., 73, 411 (1898).
<sup>10</sup> Zeit, phys. Chem., 19, 599 (18961).
<sup>11</sup> Jour. Phys. Chem., 7, 92 (1903).
<sup>11</sup> Jour. Phys. Chem., 10, 679 (1906).
<sup>14</sup> Jour. Phys. Chem., 11, 353 (1907).
<sup>15</sup> Jour. Phys. Chem., 7, 1 (1903).
<sup>16</sup> Zeit, phys. Chem., 76, 303 (1895).

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