

creases with the concentration of the iodide up to a certain point from which on the rate of liberation of iodine is twice the rate of oxidation of arsenious acid (expressing both iodide and arsenious acid in equivalents), or,

$$Rip = 2Ra, (KI \text{ excess}).$$

The rate of reduction of chromic acid (after correcting for the direct action of the iodide) is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Ra + Rip = Pac.$$

Expressing each of the three rates, *Rac* (rate of oxidation of arsenious acid by chromic acid in the absence of iodide), *Ra* (rate of oxidation of arsenious acid in the presence of iodide) and *Rip* (rate of liberation of iodine after correcting for the direct action of the chromic acid on iodide), in terms of the concentrations of the reagents, we have

$$Rac = k.As.(Cr)^{0.9}.(Ac)^{1.4}$$

$$Ra = k'.As.(Cr)^{0.9}.(Ac)^{1.4}$$

$$Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4}$$

where *k'* and *k''* depend on the concentration of the iodide. When the iodide is in excess,

$$k = 3k' = \frac{3}{2}.k''.$$

The effect of the temperature on the rates *Rac*, *Ra* (*KI excess*) and *Rip*, (*KI excess*) is the same, the coefficient being unusually small (somewhat less than 1.3).

The results may be accounted for by assuming:

(a) That arsenious acid acting on chromic acid forms slowly a primary oxide.

(b) That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.

(c) That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations: when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.