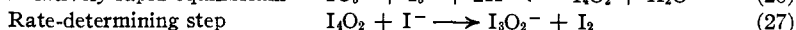
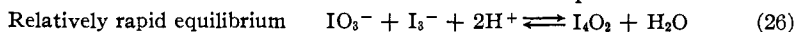


the fifth order iodate reaction which is observed in the presence of tri-iodide²



with rapid follow reactions as in (14). This mechanism is in agreement with the observation of Abel and Hilferding¹ that tri-iodide has no effect on their fourth order reaction (at low iodide concentration); but an additional assumption, that equilibrium in (27) is far to the right, seems necessary in order to explain why Skrabal found no trace of the reverse of (27) in his investigations.¹¹

The value of any proposed mechanism must be judged by its usefulness, since a rigid proof is impossible. In the present instance Skrabal's proposals, with the extensions here presented, bring into close relationship the complicated reactions of iodine and of bromine with hydroxide ion and the reverse reactions in acid solution. It is hoped that the suggested or related intermediate compounds will prove useful in future work.

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NOTE

The Atomic Weight of Chlorine. The Solubility of Silver Chloride.—

We should like to call attention to the fact that Hönigschmid and Chan,¹ in their recent work on the atomic weight of chlorine, have apparently neglected a rather important correction which affects the calculation of the Cl:AgCl ratio. Regarding the silver chloride lost in nephelometric tests, in determining the Cl:Ag ratio, the writers state: "Unter den Fällungsbedingungen enthält die klare eisgekühlte Analysenlösung bei 0° nur etwa 0.05 mg. AgCl pro Liter. Da für jede Nephelometerprobe etwa 50 cm.³, also in ganzen höchstens 150 cm.³, der Lösung entnommen wurden, konnte der durch die Probenahme bedingte Verlust an AgCl kaum mehr als 0.01 mg. betragen, war also bei der folgenden Wägung des Chlorsilbers zu vernachlässigen."

Direct nephelometric measurements of the solubility of flocculent silver chloride in pure nitric acid show that the value accepted by Hönigschmid and Chan as the solubility of silver chloride at 0° in the saturated analytical liquid *at the end-point* is entirely too low. Such measurements, made in this Laboratory in another connection, have yielded the following data.

Temp., °C.	Molarity of nitric acid	AgCl per liter, g.
0.5	0.00	0.00072
.5	.11	.00090
.5	.24	.00100
.5	.49	.00102
.5	.99	.00105

¹¹ Cf. Skrabal, Ref. 3a, p. 877.

¹ Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 315 (1927).

Although Hönigschmid and Chan do not state the concentrations of nitric acid in their analytical solutions, it seems reasonable to estimate that at least 0.001 g. of silver chloride per liter was withdrawn in the nephelometric test portions. It may be pointed out, moreover, that this is a minimum figure, because equilibrium is approached only slowly when these solutions are allowed to stand in an ice-bath. In our measurements, equilibrium was approached from the low-temperature side after completely freezing the solutions.

In order to estimate the error in the calculated atomic weight of chlorine resulting from the omission of the correction for silver chloride lost in nephelometric tests, we have recalculated the results of Hönigschmid and Chan's final gravimetric series, assuming a correction of +0.00015 g. of silver chloride in each analysis. The corrected mean of the series, 35.456, differs only a little from the value 35.457 obtained by Hönigschmid and Chan. However, since the correction affects only the gravimetric series, we can no longer regard the identical agreement of the gravimetric and nephelometric means, found by the above writers, as having any particular significance. Furthermore, the correction increases considerably the discrepancy in the results of the "complete synthesis" of the silver chloride. This can be seen from the total weights, in grams, corresponding to the eight completed experiments.

	Cl in vac.	Ag in vac.	Cl + Ag	AgCl in vac.	Difference
H. and C.	21.32439	64.88109	86.20548	86.20578	+0.00030
Recalcd.	21.32439	64.88109	86.20548	86.20698	+0.00150

It should be emphasized that the correction in question depends upon the number of nephelometric tests, which in the above case was unusually small. It seems particularly worth while to call attention to the correction because, as far as we are able to determine, it has been overlooked in other recent work from the Munich laboratory.

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