

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE  
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## CESIUM SULFATE AS A CONFIRMATORY REAGENT IN THE DETECTION OF ALUMINUM

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Cesium salts, because of their unique properties, have long been used as reagents in micro-analytical work and with the increasing demand for salts of this element together with the opening of new ore deposits, it seems certain that much more general use of its interesting properties will result both in qualitative and quantitative analysis.

The familiar aluminum tests which depend on the formation of "The-  
nard's Blue" or "lakes" with organic dyes are not altogether satisfactory,  
especially for the average student in qualitative analysis. The formation  
of a relatively copious precipitate of the insoluble cesium alum,  $\text{Cs}_2\text{SO}_4 \cdot \text{Al}_2$   
 $(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , which contains only 4.75% by weight of aluminum, is on  
the other hand a simple and decisive test. Its sensitivity will be appreci-  
ated when it is recalled that a saturated solution of cesium alum at  $0^\circ$  is  
0.00745 *M* with respect to aluminum ion, and that at  $16^\circ$  this value is but  
slightly greater, 0.0077 *M*. Concentrations of aluminum down to 0.1  
mg. per cc. are easily and rapidly detected.

### Procedure

The supposed aluminum hydroxide, separated in the usual manner from  
the other Group III metals, is dissolved in 1–5 cc. of hot 3 *M* sulfuric acid  
by repeatedly pouring the acid through the filter. (If the precipitate is  
large, it is more convenient to remove some of it and dissolve in an evapo-  
rating dish.) The resulting aluminum sulfate solution is cooled and 0.5–1  
cc. of approximately 0.25 *M* cesium sulfate is added. On scratching the  
walls of the test-tube with a stirring rod, the dense white cesium alum  
separates and rapidly settles.

**Time Required for Precipitation.**—Due to the great tendency of  
cesium alum solutions to remain supersaturated, the following rough classi-  
fication has been made

Concn. of Al ion in mg. per cc.	5 and greater	1–5	0.1–1
Time for precipitation	instantaneous	1 minute	3 minutes

**Interfering Elements.**—Although cesium has a great tendency to form  
double salts with many elements, only bismuth is likely to be troublesome.  
In practice this possibility of confusion may be eliminated by adding one  
drop of concd. hydrochloric acid to a portion of the white precipitate.  
Warm and add 1 cc. of hydrogen sulfide water. A brown precipitate of  
bismuth sulfide will indicate the presence of that element. Ferric and  
chromic alums are much more soluble than the aluminum alum. Beryl-

lithium and magnesium do not interfere. The elements lanthanum cerium, praseodymium, neodymium, erbium, yttrium, thorium, zirconium (and probably hafnium) form more soluble double cesium sulfates or form them much more slowly than aluminum.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## AN OXIDE OF IODINE, $I_2O_2$ . AN INTERMEDIATE COMPOUND

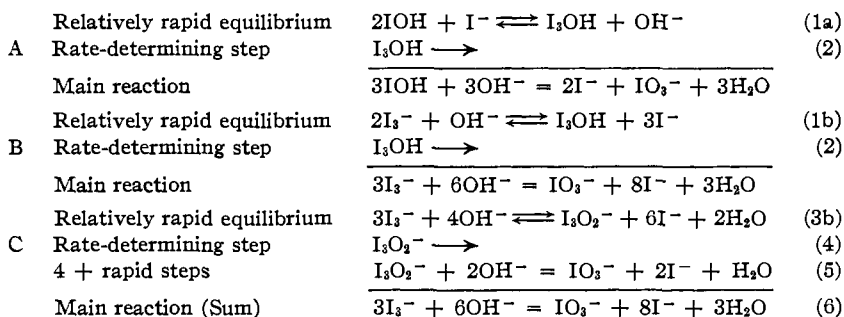
BY WILLIAM C. BRAY

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The recent experimental proof by Abel and Hilferding<sup>1</sup> that the reaction between iodate and iodide ions in acid solution, long known as a fifth order reaction,<sup>2</sup> is of the fourth order at a low iodide concentration, has led me to reexamine the series of investigations of Skrabal<sup>3</sup> on the rate of formation of iodate and iodide from iodine and hydroxide ion. Skrabal presented strong evidence that  $HI_3O$  and  $I_3O_2^-$  exist as intermediate compounds in this reaction, and that  $HI_3O$  is a loose addition compound of iodine and hypiodous acid. He also pictured  $I_3O_2^-$  as a similar compound of iodine and iodite ion. The present analysis has led to the conclusion that  $H_2I_2O_3$  and  $I_2O_2$  also exist as intermediate compounds, and that  $I_3O_2^-$  is really an addition compound of  $I_2O_2$  and iodide ion.

Skrabal succeeded in demonstrating that the results of his rate measurements could be represented by three rate laws, A, B and C, and postulated the following mechanisms



<sup>1</sup> Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

<sup>2</sup> (a) Dushman, *J. Phys. Chem.*, **8**, 453 (1904); (b) Skrabal, *Z. Elektrochem.*, **28**, 224 (1922); **30**, 109 (1924); (c) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926).

<sup>3</sup> Skrabal, (a) *Monatsh.*, **32**, 815-903 (1911); (b) *Oesterr. Chem.-Ztg.*, No. 11 (1913); (a) is the fifth paper of a series of twelve, 1907-1916, on hypohalous acids and hypophalites, and (b) is a general discussion of the stoichiometric reactions of iodine isolated and studied in his investigations.