

been measured using the following concentrations of sulfuric acid: 85.52, 89.53, 91.49, 92.78, 94.40 and 96.69% at 15, 25, 35 and 45°.

2. The temperature coefficients have been given. They decrease in magnitude as the velocity constant increases.

3. The values for  $E$  (critical increment) have been calculated and found to be nearly equal for all concentrations at the temperature intervals 25°/15°, 35°/25° and 45°/35°.

4. For equal concentrations of sulfuric acid, the effect of small quantities of water becomes more marked with increase in temperature.

5. No irregularities in velocity constants or temperature coefficients were observed in the temperatures and concentrations studied.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## THE USE OF POTASSIUM IODATE IN BACK TITRATION FOR THE DETERMINATION OF THE HYPOCHLORITE CONTENT OF SOLUTIONS

By JOHN R. LEWIS AND R. F. KLOCKOW

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Volumetric iodate methods for the analysis of a variety of substances have been collected and published by Jamieson.<sup>1</sup> While searching the literature for methods of analyzing sodium hypochlorite solutions, it occurred to the authors that potassium iodate may also be used here. When a standard arsenite, thiosulfate or iodide solution was used in excess to reduce the hypochlorite, it was found that the excess could be determined by titration with potassium iodate according to the method described by Jamieson for the determination of hydrogen peroxide.

**Method I (Sodium Arsenite Method).**—To a known excess of standard arsenite is added a measured volume of hypochlorite. The unoxidized excess is then titrated with 0.1  $N$  iodate in the presence of at least 12% hydrochloric acid. The results are accurate in the presence of small amounts of nitrate or chlorate.

**Method II (Sodium Thiosulfate Method).**—This method is based upon the fact that sodium hypochlorite oxidizes sodium thiosulfate to sulfate in an acid solution.<sup>2</sup> The titration mixture should be cooled in an ice-bath before adding the iodate. It makes no difference whether the hypochlorite is added to the acid or neutral solution of the thiosulfate. Results are not concordant in the presence of chlorate.

<sup>1</sup> George S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., Inc., New York, 1926.

<sup>2</sup> Dienert and Wandenbulcke, *Ann. chim. anal. chim. appl.*, **2**, 106 (1920).

**Method III (Iodide Method).**—In this method the hypochlorite is reduced with potassium iodide. The mixture should be cooled in ice water before titrating with iodate. Chlorate interferes.

TABLE I  
RESULTS

No.	NaClO by Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> -I method, g.	NaClO by Method I, g.	NaClO by Method II, g.	NaClO by Method III, g.
1	0.0549	0.0545	0.0546	...
2	.0397	.0396	.0394	...
3	.0134	.0132	.0836	...
4	.0286	.0285	.0285	...
5	.0687	.0689	.0686	...
6	.0667	...	...	0.0664
7	.0694	...	...	.0693
8	.0675	...	...	.0672

### Summary

Hypochlorite was determined by reducing with an excess of arsenite, thiosulfate or iodide and titrating the excess with iodate.

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## THE GASEOUS EXPLOSIVE REACTION AT CONSTANT PRESSURE. THE EFFECT OF INERT GASES<sup>1</sup>

By F. W. STEVENS

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### Thermodynamics

The effect of inert gases upon the thermodynamic equilibrium of gaseous explosive reactions has received extended consideration from Nernst and his pupils,<sup>2</sup> who employed in their investigations a spherical bomb of constant volume with central ignition. This series of studies extended to temperatures of over 3000° Abs. and formed part of the most extensive investigation of gaseous reactions involving the equilibrium products of combustion, carbon dioxide and water vapor that has yet been carried out. "No other chemical equilibrium has so far been investigated by so many methods which can also be controlled at the same time by thermodynamic calculations. . . . A specially high value must be attached to explosion methods since by suitable variations of the experimental conditions it enables both the specific heats and the equilibrium to be determined."<sup>3</sup>

<sup>1</sup> Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

<sup>2</sup> (a) Pier, *Z. Elektrochem.*, **15**, 536 (1909); (b) **16**, 897 (1910); (c) Bjerrum, *ibid.*, **17**, 731 (1911); (d) **18**, 101 (1912); (e) *Z. physik. Chem.*, **79**, 513, 537 (1912); (f) **81**, 284 (1913); (g) Siegel, *ibid.*, **87**, 641 (1914).

<sup>3</sup> Nernst, "Theoretical Chemistry," Macmillan Company, New York, 10th ed., 1923, p. 783.