

The importance of considering the entropy of activation is well illustrated by the  $\text{BaCl}_2$  and  $\text{LaCl}_3$  additions in Reaction I. In spite of an increase of 1800 calories in  $E_{\text{act.}}$ , the velocity nevertheless increases due to an increase in  $S_{\text{act.}}$  as shown by the marked increase in  $B$ .

Reaction III and the rearrangement of acetylchloroaminobenzene are being studied over wider ranges of temperature for a more convincing test of the conclusions drawn.

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NEW YORK, N. Y.

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RECEIVED FEBRUARY 17, 1933      PUBLISHED APRIL 6, 1933

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#### MODIFICATION OF THE WILLARD-WINTER METHOD FOR FLUORINE DETERMINATION

*Sir:*

The use of standard thorium nitrate solutions for the titration of fluorine, as developed by Willard and Winter [*Ind. Eng. Chem., Anal. Ed.*, **5**, 7-10 (1933)], affords an accurate method for the determination of soluble fluorides. However, the end-point of the titration, when the amount of the zirconium-alizarin indicator specified by the writers is being used, is so faint as to be difficult to detect. Larger amounts of indicator cannot be employed, especially when one is titrating small quantities of fluorine, since zirconium combines with fluorine.

This difficulty can be avoided by the use of a 0.05% aqueous solution of sodium alizarin sulfonate alone as the indicator. The procedure is essentially the same as that employed by Willard and Winter. Three drops of the indicator solution are added to 40 cc. of solution containing 20 cc. of alcohol. Dilute hydrochloric acid (1:50) is added dropwise until the solution is colored yellow. A further drop of acid is then added. The end-point of the titration is recognized by the appearance of a faint, permanent pink color due to the formation of the thorium lake. The use of an arbitrary reference solution of the lake with a slight pink color makes for more accurate results, because the titrated solution shades from yellow to pink as the end-point is approached. The procedure succeeds best with fractional quantities of a milligram of fluorine, since the troublesome adsorption of the dye and lake on the precipitated thorium fluoride is rendered less noticeable.

The results tabulated below were obtained when solutions of sodium fluoride were titrated with a thorium nitrate solution of such strength that 1.0 cc. was equivalent to 0.2 mg. of the fluorine. The microburet readings were rounded off to the nearest 0.005 cc., and 0.030 cc. was subtracted from each of the readings to account for the thorium required to form the lake. The analyst did not know the fluorine content of the solutions marked with an asterisk.

Th(NO <sub>3</sub> ) <sub>4</sub> , cc.	F Calcd., mg.	F Found, mg.	Th(NO <sub>3</sub> ) <sub>4</sub> , cc.	F Calcd., mg.	F Found, mg.
0.260	0.050	0.052	0.990	0.200	0.198
.245		.049	1.020		.204
.520	.100	.104	1.000	.201*	.200
.505		.101	1.155	.230*	.231
.760	.150	.152	1.490	.300	.298
.865	.175*	.173	2.000	.400	.400

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RECEIVED MARCH 8, 1933

PUBLISHED APRIL 6, 1933

### A NEW BAND IN THE WATER VAPOR DISCHARGE

*Sir:*

In a spectrographic study of the electrodeless discharge in water vapor the writers have observed a band of moderate intensity with a head of wave length 3564 Å. This band is degraded toward the red and appears to have the structure of a hydride. It does not belong to any known system of hydroxyl bands and may prove to be due to OH<sup>+</sup>. Other fainter bands were also observed which have not been measured accurately or identified. The analysis of these bands is being carried out under the direction of Professor F. W. Loomis of the Department of Physics.

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RECEIVED MARCH 20, 1933

PUBLISHED APRIL 6, 1933

## NEW BOOKS

**Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, de Biologie et de Technologie.** (Annual Tables of Constants (A T C) and Numerical Data, Chemical, Physical, Biological and Technological.) Published under the Patronage of the International Research Council and of the International Union of Chemistry. American Agents, McGraw-Hill Book Co., Inc., 330 West 42d St., New York, 1931-1932. Vol. VIII, 2 parts (1927-1928), 2706 pp. Vol. IX (1929), 1607 pp.; Index to Vol. IX, 124 pp. 22 × 28 cm. Price, cloth, Vol. VIII, \$20.00; Vol. IX, \$16.00.

With the appearance of Volume IX for 1929 and of Volume VIII in two parts covering 1927-1928, Dr. Marie and the International Committee have finally completed the Herculean task of bringing the Annual Tables up to date, after the serious interruption and delay incident to the World War. Volume IX was issued at the end of 1931, and its Index a few months later. This resumption of prompt publication is of great importance to the scientific world, and Dr. Marie and the Committee are to be congratulated