

the X-ray data as the scattering power of these atoms is too low in comparison with that of the tungsten atoms. The arrangement of the latter, however, is very similar to that derived by Hägg<sup>2</sup> for the cubic sodium tungsten bronze of perovskite type. This fact suggests that the two structures are closely related, and leads to the following atomic configuration of the tetragonal bronze, which corresponds throughout to plausible interatomic distances:

Cell content:  $2 \text{Na}_x\text{WO}_3$   
 Space-group:  $D_{4h}^7 - P4/nmm$   
 2 W in 2(c):  $0\frac{1}{2}z, \frac{1}{2}0\bar{z}$   $z = 0.435$   
 $2x\text{Na}$  in 2(a):  $000, \frac{1}{2}\frac{1}{2}0$   
 2 O in 2(c):  $0\frac{1}{2}z, \frac{1}{2}0\bar{z}$   $z \approx 0.935$   
 4 O in 4(e):  $\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{1}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}$

The structure may be described as built up of deformed  $\text{WO}_6$  octahedra, joined by sharing corners. The alkali metal atoms are statistically distributed and occupy approximately 10 per cent of the major interstices of the lattice. (It must be emphasized that this scheme presupposes the unit cell dimensions and symmetry of the actual structure to be identical with those of the tungsten lattice.)

The tungsten atoms form puckered networks extending parallel to the  $ab$  plane, by being a little displaced alternately  $+ 0.25\text{Å}$  and  $- 0.25\text{Å}$  in the direction of the  $c$  axis. In this respect which constitutes the difference from a lattice of perovskite type, the structure is reminiscent of the tungsten trioxide structure of deformed  $\text{ReO}_3$ -type, the metal atoms of which show similar displacements parallel to two of the axes of the cubic substructure cell ( $\pm 0.23\text{Å}$  and  $\pm 0.24\text{Å}$  respectively)<sup>3</sup>. It is noteworthy that another tetragonal sodium tungsten bronze,  $\text{Na}_x\text{WO}_3$  ( $x \approx 0.3$ ), of complicated structure also contains puckered networks of tungsten atoms<sup>4</sup>.

These structural relationships evidently demonstrate the character of the bronzes

of degenerated perovskite type to be a distinct intermediate state in the transitions with decreasing alkali metal content from the cubic sodium<sup>2</sup> and lithium<sup>5</sup> bronzes of perovskite type to tungsten trioxide.

The author is indebted to Miss Birgitta Blomberg for her valuable assistance. The work has been supported by a grant from the Swedish Natural Science Research Council, whose assistance is gratefully acknowledged.

1. Magnéli, A., and Blomberg, Birgitta *Acta Chem. Scand.* In print.
2. Hägg, G. *Z. physik. Chem.* (B) **29** (1935) 192.
3. Brækken, H. *Z. Krist.* **78** (1931) 484.
4. Magnéli, A. *Arkiv Kemi* **1** (1949) 213.
5. Magnéli, A., and Nilsson, R. *Acta Chem. Scand.* **4** (1950) 398.

Received May 5, 1951.

## Estimation of Xylocaine\* by Nitration

BERTIL ORTENBLAD

Central Laboratories, Astra,  
Södertälje, Sweden

Comprehensive experiments have shown that Xylocaine ( $\alpha$ -diethylamino-2,6-acetoxylicide) can be nitrated in a simple manner with analytical reproducibility. However the nitration conditions must be rigidly controlled since the course of the reaction is easily affected by variations in the reagent and the temperature employed. Nitration at  $80^\circ\text{C}$  with one part of conc. nitric acid and five parts of acetic acid seems to be most suitable. Hydrogenation of the nitration product is subject to similar limitations. The method would appear to be specially suitable for estimation of Xylocaine in small amounts, in dilute solutions and possibly also in biological material. The procedure and applicability of the method are being further investigated at present.

\* Regd. trade mark.

It has recently come to my notice that this problem has also been independently studied at Statens Farmaceutiska Laboratorium, Stockholm, Sweden, by A. Brunzell and H. Seidlitz; by a coincidence it was established that both investigations have led to fundamentally the same result.

Received December 28, 1950.

### On the Kinetics of Formation of Precipitates of Sparingly Soluble Salts \*

J. A. CHRISTIANSEN and ARNE E. NIELSEN

*Institute of Physical Chemistry, University of Copenhagen, Copenhagen, Denmark*

To get information regarding the mechanism of precipitation we have made preliminary experiments on the systems bariumchloride + sulphuric acid and silver nitrate + potassium chromate.

For the more concentrated solutions (0.01 molar) we used a flow method according to Roughton's principle<sup>1</sup>. Three glass tubes, two for inflow of the two component solutions and one for outflow of the mixture were cemented into a "crosshead" from perspex, containing the mixing chamber and adjacent channels for inflow and outflow. The outflow tubing had a bore of about 2 mm.

In the outflow tube the place and thus the time of occurrence of visible precipitation could be observed. In that way precipitations occurring in times after the mixing from  $10^{-3}$  seconds to about  $10^{-1}$  seconds could be observed. By stopping the flow and noting the time of appearance of visible precipitation observations could be

\* The content of the following three notes was given in a lecture to a joint meeting of Kemiska Föreningen, Lund, Sweden and Kemisk Forening, København, held in Copenhagen May 19, 1951.

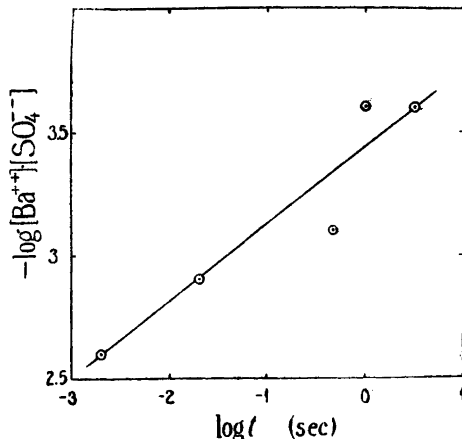


Fig. 1. The diagram represents the relation between the product of the concentration of barium ions and sulphate ions and the time of visible precipitation. Dekadic logarithms, time in seconds, concentration in moles/liter.

taken in times from about 1 to about 10 seconds, while longer times than that could be observed simply by mixing of the two solutions in a beaker.

The scale of times thus extends over an interval of 4 to 6 powers of ten.

The times for visible precipitation could only be determined to within a factor of

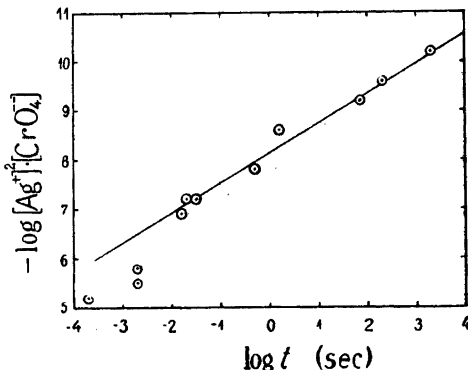


Fig. 2. The diagram represents the relation between the product of the concentration of silver ions (squared) and of chromate ions and the time of visible precipitation.