

Muslim University, Aligarh, for kindly taking the microphotographs.

V. T. CHIPLONKAR.

Physics Department,  
Benares Hindu University,  
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<sup>1</sup> W. Wien, 'Kanalstrahlen', *Handbuch der Experimental Physik*, 1927, Band 14, 443.

<sup>2</sup> *Ibid.*, p. 693.

<sup>3</sup> N. D. Smith, *Phys. Rev.*, 1936, 49, 345.

<sup>4</sup> G. Herzberg, *Ann. d. Physik.*, 1927, 84, 553.

<sup>5</sup> W. Finkelnburg, 'Kontinuierliche Spektren' *Struktur und Eigenschaften der Materie*, Band 20, Julius Springer, 1938, p. 184.

#### GRAVIMETRIC DETERMINATION OF MANGANESE WITH 8-HYDROXY- QUINOLINE

BERG<sup>1</sup> showed that manganese could be precipitated quantitatively by means of 8-hydroxyquinoline ("Oxine") as a dull yellow crystalline compound with the composition  $Mn(C_9H_6ON)_2 \cdot 2H_2O$ . The precipitation was carried out either from (1) a neutral or weakly acid solution containing sodium acetate and a small amount of sulphite or hydroxylamine by adding an excess of an alcoholic solution of the reagent, or (2) from a mineral acid solution containing an excess of an acetic acid solution of the reagent by adding dilute ammonia until weakly alkaline. The precipitates obtained by both methods, however, could not be satisfactorily dried to constant weight since at 110° C. drying was very slow and above this temperature appreciable decomposition occurred. The gravimetric determination was, therefore, carried out by Berg (*loc. cit.*) by igniting the precipitate to the oxide,  $Mn_3O_4$  with oxalic acid and weighing.

Raikow and Tischkow<sup>2</sup> showed that the composition of the ignited tetroxide depends on the temperature and the nature of the atmosphere surrounding the precipitate during the ignition. Further the procedure adopted by Berg for the gravimetric determination suffers from the fact that no advantage is taken of the precipitation

of manganese as the heavier oxyquinolate molecule.

During the present investigation it was found that the heat stability of the precipitates during drying depended considerably on the method of precipitation. While precipitates obtained by Berg's first method were easily decomposed at temperatures higher than 110° C., those obtained by the second method were quite stable at temperatures as high as 150–170° C. Prolonged drying (20 hours) at 150° C. did not produce any decomposition in a large number of cases studied with amounts of manganese varying from 0.3 to 60 mg. In a few cases, however, a slight superficial discolouration of the precipitates was observed but this was not even when dealing with the small amounts of manganese. It was also found that discolouration did not occur when the drying was carried out in the presence of sulphurous acid. The temperature (170° C.) at which the precipitates were quite stable and no weight loss was appreciable. A temperature of 150° C. was, however, considered to be the most suitable for drying. Constant weight of the precipitates was attained in two to three hours at this temperature and the composition of the dried precipitates corresponded to  $Mn(C_9H_6ON)_2$  containing 16.03 per cent. manganese.

The influence of large amounts of ammonium chloride, sodium chloride and ammonium oxalate, as occur in the filtrate from "lime and strontia" in rock analysis, on the precipitation of manganese was also studied with a view to adapt the "oxine" method for the precipitation of magnesium and residual manganese in rock analysis. It was found that both manganese and magnesium could be precipitated together quantitatively adopting Berg's second method provided ammonium salts, and oxalic acid which interfered with the precipitation of magnesium as the oxyquinolate, were removed by the nitric acid method.<sup>3,4</sup> The precipitates thus obtained were dried to constant weight at 150° C. and weighed. To determine the manganese in these precipitates, the weighed

precipitate was dissolved in nitric acid (1:1), the solution evaporated to dryness in a platinum dish and the organic matter ignited. The residue was dissolved in concentrated nitric acid and the manganese determined colorimetrically by the periodate method. Satisfactory results were obtained for both manganese and magnesium.

The above work was done by the author in collaboration with H. F. Harwood and L. S. Theobald of the Imperial College of Science and Technology, London. Details will be published later.

K. NEELAKANTAM.

Department of Chemistry,  
Andhra University,  
Waltair,  
December 17, 1940.

<sup>1</sup> Berg, *Z. anal. Chem.*, 1929, **76**, 191.

<sup>2</sup> Raikow and Tischkow, *Chem. Ztg.*, 1911, **35**, 1013.

<sup>3</sup> Hillebrand and Lundell, *Applied Inorganic Analysis*, 1929, p. 119.

<sup>4</sup> Miller and McLennan, *J. Chem. Soc.*, 1940, 653.

#### ON THE VELOCITY OF SOUND IN AND CHEMICAL REACTIVITY OF BROMINE AND IODINE

THE velocity of sound in metallic elements has been found to be dependent upon the atomic frequency and the least distance separating the atoms.<sup>1</sup> This least distance between the atoms concerned determines the chemical reactivity and approximates to "critical atomic approach value" for any type of action.<sup>2</sup> The direct formation of bromides and iodides suggest for the 'critical atomic approach' values which may be taken to be equal to the least distance separating the atoms of these two elements. With these values of least atomic distances and author's values of atomic frequencies, attempt may here be made to compute the velocities of sound in these non-metallic elements by applying the author's formula for the case of metals.

Element	Atomic Frequency	Distance of closest approach of atoms	Valency	Constant	S. calc.	S. obs.
Bromine	2.76 <sup>(4)</sup>	1.88 <sup>(5)</sup>	1	10	131.1	135.0
Iodine	2.1 <sup>(4)</sup>	2.12 <sup>(5)</sup>	1	10	113.1	107.7

It would be evident from the above table that the values so obtained are comparable with those observed.<sup>3</sup> It would thus appear that the author's formula for the calculation of velocities of sound in metallic elements may be extended to such calculation at least in two non-metals. Further, there would appear to be a relationship between the velocity of sound in bromine and iodine and the 'critical atomic approach values' for the direct formation of bromides and iodides. So velocity of sound appears to be significant for bromide and iodide formation.

The formula proposed for the calculation of velocity of sound in metallic elements may be represented thus

$$S = L \left\{ \left( \frac{1}{2\pi} \sqrt{K} \sqrt{\frac{P-V}{V} \cdot \frac{Ze^2}{r^3} \cdot \frac{N}{M}} \right) \times \left( f_2 \times f_1 (V) \frac{P}{V_i \times d^{k_1}} \right) \right\}$$

where S is the velocity of sound in metallic elements, L a constant having value 2.54;

$\left( \frac{1}{2\pi} \sqrt{K} \sqrt{\frac{P-V}{V} \cdot \frac{Ze^2}{r^3} \cdot \frac{N}{M}} \right)$  the atomic frequency<sup>4</sup> and  $\left( f_2 \times f_1 (V) \frac{P}{V_i \times d^{k_1}} \right)$  the distance of the closest approach of atoms.<sup>5</sup>

In the factors  $\left( \frac{1}{2\pi} \sqrt{K} \sqrt{\frac{P-V}{V} \cdot \frac{Ze^2}{r^3} \cdot \frac{N}{M}} \right)$  and  $\left[ f_2 \times f_1 (V) \frac{P}{V_i \times d^{k_1}} \right]$ , P represents parachor, V the atomic volume, Z the valency, M atomic weight, e the elementary charge, N Avogadro's number, V the ionisation potential, K and  $\sqrt{K}$  constants having the values 0.925 and  $0.415 \times 10^{12}$ , and  $f_2 \times f_1 (V)$  a constant depending upon valency having the dimension  $\frac{M^{1/2}}{L^{1.575} \times T}$  which in the present instances takes the value .615.<sup>5</sup>