

which the tertiary hydroxyl is then partially eliminated with the production of cholestanol-3. It is probable that the formation of the primary reduction product would have taken precedence over the side reactions if the experimental conditions had permitted a shortening of the reduction period.

The several examples now at hand permit the generalization that when an ethylene oxide ring is opened by hydrogenation the hydroxyl group formed will be attached to the carbon atom carrying the smaller number of hydrogen atoms,<sup>9</sup> as one would expect on theoretical grounds.

### Experimental

Two hundred mg. of palladium catalyst in acetic acid was saturated with hydrogen, and a solution of 300 mg. of cholesterol  $\alpha$ -oxide, m. p. 141°, in acetic acid was added. After three hours of shaking only two-thirds mole (10 cc.) of hydrogen had been absorbed. Intermittent shaking was continued for two days, and the total hydrogen uptake was 18 cc. (1.2 moles). After removal of the catalyst the acetic acid was removed by vacuum distillation and the residue acetylated at room temperature overnight with pyridine-acetic anhydride. The total acetylated reaction product was dissolved in hexane and chromatographed on a column of alumina 1  $\times$  15 cm. Elution was carried out with hexane, then with hexane-benzene mixtures, and finally with benzene. The hexane fractions yielded 85 mg. After two recrystallizations from methanol the m. p. was 109–110°. The m. p. of a mixture with cholestanol-3 acetate was not depressed.

*Anal.* Calcd. for C<sub>29</sub>H<sub>50</sub>O<sub>2</sub>: C, 80.86; H, 11.70. Found: C, 80.80; H, 11.77.

The combined residues from the hexane-benzene (2/1) mixtures weighed 120 mg. After several recrystallizations the m. p. was constant at 181°.

*Anal.* Calcd. for C<sub>29</sub>H<sub>50</sub>O<sub>3</sub>: C, 77.97; H, 11.28. Found: C, 77.81; H, 11.08.

Twenty-five mg. of the diol acetate was hydrolyzed with methanolic potassium hydroxide. The diol had a m. p. of 216–217°. Chinaeva and Ushakov<sup>7</sup> give a m. p. of 201° for the diol and 177° for the acetate.

The residue from the benzene fractions weighed 75 mg. After several recrystallizations from methanol the m. p. was 165–167°. The m. p. of a mixture with authentic  $\alpha$ -cholestanetriol-3,5,6 diacetate was not depressed.

*Anal.* Calcd. for C<sub>31</sub>H<sub>52</sub>O<sub>5</sub>: C, 73.77; H, 10.39. Found: C, 73.67; H, 10.63.

The triol was prepared by hydrolysis of the diacetate, m. p. 227–230°. The m. p. of a mixture with an authentic sample was not depressed.

THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH  
DIVISION OF ORGANIC CHEMISTRY  
NEW BRUNSWICK, N. J. RECEIVED AUGUST 10, 1942

(9) Krassusky, *Chem. Ztg.*, **31**, 704 (1907), found that a similar rule applies when the alkene oxide ring is opened with ammonia to form  $\alpha$ -amino alcohols.

### Revised Constants for the Debye-Hückel Theory

BY H. I. STONEHILL AND M. A. BERRY

Using the newer values of certain fundamental constants, *viz.*,  $e$  (electronic charge) =  $4.803 \times 10^{-10}$  e. s. u.,  $k = 1.379 \times 10^{-16}$  erg/°C.,  $N = 6.028 \times 10^{23}$ ,  $T_0$  (ice point) =  $273.18^\circ\text{K.}$ ,<sup>1</sup>  $D$  (dielectric constant of water at 25°) =  $78.54$ ,<sup>2</sup> it may be calculated that the values of  $h$  and  $g$  in the first term of the Debye-Hückel expression for the log of the activity coefficient of a  $z_1:z_2$  valent electrolyte in aqueous solution at 25°

$$\log \gamma = \frac{-hz_1z_2\sqrt{I}}{1 + ga\sqrt{I}} - \log(1 + 0.018\sum m_i)$$

are  $h = 0.5103$  and  $g = 0.3290 \times 10^8$ .

The older values,  $e = 4.774 \times 10^{-10}$ ,  $k = 1.372 \times 10^{-16}$ ,  $N = 6.061 \times 10^{23}$ ,  $T_0 = 273.1^\circ\text{K.}$ ,<sup>3</sup> lead to  $h = 0.5065$ ,  $g = 0.3287 \times 10^8$ . Harned and Robinson in two recent publications<sup>4,5</sup> employed the values  $h = 0.5065$ ,  $g = 0.3288 \times 10^8$  and  $h = 0.5056$ ,  $g = 0.3288 \times 10^8$ . While the value of  $g$  is practically unchanged, there are discrepancies of 1.0 and 0.8% between 0.5103 and the two values of  $h$  used by Harned and Robinson, leading to corresponding discrepancies in the first term of the Debye-Hückel equation. This term is the most important one even in extended forms of the equation containing arbitrary linear, quadratic or other additional functions of concentration, at least up to about  $I = 1.0$ . Thus a 0.9% error in  $h$  corresponds to an approximately equal error in  $\log \gamma$ . A 0.9% error in  $\log \gamma$  corresponds to % errors in  $\gamma$  of 0.1, 0.2, 0.3, 0.5, 0.7, 0.8, 1.1, 1.5, 2.1 when  $\gamma$  is, respectively, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2 and 0.1. Hence any equation purporting to give activity coefficients with an error not exceeding these limits should use the newer value of  $h$ . This will not affect the work of Harned and Robinson<sup>5</sup> since they only claimed an accuracy of 0.3% in  $\gamma$  where  $\gamma$  was always greater than 0.8; but there are many other calculations which will need revision, *e. g.*, the linear relation between  $\log a$  and  $\log B$  discovered by Harned and Robinson<sup>4</sup> for the alkali halides may not exist if values of  $a$  and  $B$  are recalculated with the newer value of  $h$ .

The authors on February 26, 1942, furnished the following supporting information: "Take the case of a 1:1 valent

(1) Childs, "Physical Constants," London, 1939.

(2) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(3) "International Critical Tables."

(4) Harned and Robinson, *Chem. Rev.*, **28**, 419 (1941).

(5) Harned and Robinson, *Trans. Faraday Soc.*, **37**, 302 (1941).

electrolyte at concentration  $c$  (equal to the ionic strength). Then

$$\log f = \frac{-h \sqrt{c}}{1 + ga \sqrt{c}} + Bc$$

Assume a fixed value for  $c$  and thus for  $\log f$ . To find how a slight change in the value of  $h$  will affect  $a$  and  $B$ , we differentiate, treating  $g$  as a constant, since its value has been shown to remain practically unchanged when new fundamental constants are used. Thus

$$0 = -dh \frac{\sqrt{c}}{1 + ga \sqrt{c}} + \frac{h \sqrt{c}}{1 + ga \sqrt{c}} \cdot \frac{g \sqrt{c}}{1 + ga \sqrt{c}} da + dB$$

Hence

$$dh = \frac{hg \sqrt{c}}{1 + ga \sqrt{c}} da + \sqrt{c}(1 + ga \sqrt{c})dB \quad (1)$$

Robinson and Harned's proposed logarithmic relation between  $a$  and  $B$  is

$$\log B = 14 \log a - 9.75$$

which gives upon differentiation

$$dB/B = 14da/a \quad (2)$$

Now take a definite though hypothetical example chosen for simplicity, namely, an electrolyte for which  $ga = 1$ , or  $a = 1/g = (1/0.3289) \times 10^{-3} = 3.04 \times 10^{-3}$ . Put  $h = 0.5065$  (the value at  $25^\circ$  used by Robinson and Harned), and  $dh = 0.0038$  (the difference between 0.5065 and the newer value 0.5103). Applying equation (1) to a convenient pair of arbitrarily chosen concentrations,  $(0.1)^2$  and  $(0.3)^2$ , which are low enough for the theory to apply, we obtain

$$0.0038 = \left[ da \times \frac{0.5065 \times 0.1 \times 0.3289 \times 10^3}{1.1} \right] + [dB \times 0.1 \times 1.1]$$

and

$$0.0038 = \left[ da \times \frac{0.5065 \times 0.3 \times 0.3289 \times 10^3}{1.3} \right] + [dB \times 0.3 \times 1.3]$$

whence

$$da = 0.634 \times 10^{-8}$$

$$dB = -0.0528$$

Results such as these would, of course, have to be obtained for various pairs of concentrations and then averaged by the method of least squares. The preservation of the logarithmic relation between  $a$  and  $B$  requires, as shown by equation (2), that any increase in  $a$  should be accompanied by an increase in  $B$ , whereas we have just shown that an increase in  $a$  due to a change in the value of  $h$  is accompanied by a very great decrease in  $B$  (for alkali and hydrogen halides  $B$  is of the order 0.01 to 0.2, so  $dB$  is relatively important).—THE EDITOR.

CHEMISTRY DEPARTMENT  
TECHNICAL COLLEGE RECEIVED DECEMBER 11, 1941  
BRADFORD, YORKSHIRE, ENGLAND

### Crude Boron. Analysis and Composition

BY EARL H. WINSLOW AND HERMAN A. LIEBHAFSKY

When "pure" boron bought commercially began to vary widely from one lot to the next, we planned

analyses to discover why. The chemical literature was not very helpful, and we have consequently explored several ways in which such analyses can be done. The results for three commercial borons will be given below; but the experimental methods will be outlined only, and detailed literature references will be omitted. This procedure is justified because our results are not exact, because the methods may need modification to fit the particular boron being examined, and because much of the literature on elementary boron is unsatisfactory. In judging this literature, however—and in judging our work—the complexity of the boron problem should not be forgotten.

**Total Boron by Fusion.**—The sodium peroxide fusion was done in a Parr bomb with 12 g. of sodium peroxide and 1 g. of sucrose. For the carbonate-nitrate fusion, the sample was mixed in a platinum crucible with 12 g. of the fusion mixture (by weight, 2 parts sodium carbonate, 1 part potassium nitrate) and covered with 6 g. of the mixture. The crucible was heated for two hours on a hot-plate near  $700^\circ$ , then by a free flame until appreciable melting had occurred. Attack of the platinum was slight.

The fusion mixtures were dissolved and neutralized; the solutions were titrated for boron by the usual method except that a glass electrode—which is very convenient for the purpose—was used. The maximum value of  $\Delta pH/\Delta cc.$  was taken as the end-point. Any precipitate was dissolved and reprecipitated; the resulting solution was titrated for boron also. Table I shows that fine, black powders sold commercially as pure boron may contain less than 80% of that element. We have found chlorination to be an effective tool for studying the impurities present.

TABLE I

| PER CENT. TOTAL BORON BY FUSION OF DRIED SAMPLES | Boron I | "Pure" Boron       | "99%" Boron |
|--|---------|--------------------|-------------|
| Sodium Peroxide Fusion                           | 70      | 77 <sup>a</sup> 76 | 71 72       |
| Carbonate-Nitrate Fusion                         | 65      | 71                 | 75          |

<sup>a</sup> Result from 100-mg. sample; all other samples near 25 mg.

**Rapid Chlorination.**—Very dry chlorine was passed into a vertical quartz test-tube on the bottom of which rested a quartz bucket containing the boron. A snugly fitting glass seal, through which the chlorine tube passed, prevented air or water from entering the test-tube against the issuing stream of chlorine and (later) of boron trichloride. The temperature of the sample was raised whenever glowing and fuming at a lower temperature had ceased. When no further reaction could be observed, the residues (sometimes white, sometimes gray) were weighed and examined; iron and aluminum were determined in the sublimate on the walls of the test-tube. The quartz buckets changed neither in weight nor appearance. Experiments with boric oxide showed that appreciable volatilization of this substance was not to be expected at  $725^\circ$ , the maximum temperature for these chlorinations.