POLARISTROBOMETRIC-CHEMICAL ANALYSIS.

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†Translated by J. F. GEISLER.

INTRODUCTORY.

In determining the rotatory power of optically active substances in solution the following factors are of practical bearing :

a. The observed angular rotation of a ray of light (usually D) by a solution at a definite temperature (generally 20°).

l. The length of the tubes used (in decimeters).

d. The sp. gr. of the solution (generally determined at 20°, calculated upon water at 4°).

p. The %, *i.e.* the weight of active substance in 100 parts by weight of the solution.

q. The % of optically inactive substance.

c = pd the concentration, *i.e.* the number of grammes of active substance in 100 c. c. of the solution.

From these the sp. rotatory power is found by

$$([a] = \frac{100a}{\mathrm{l\,c}} = \frac{100a}{\mathrm{l\,p\,d}} \qquad (1)$$

which gives the angular rotation which a column of the solution 1 dm. in length would cause, if each c. c. contained 1g of the optically active substance.

The sp. rot. power is affected not only by the wave length of the ray of light and the temperature, but usually also by the nature of the solvent as well as the percentage (p) and the concentration (c).

The increase or decrease of the specific rotation of nearly all optically active substances, which is shown by the varying composition of the solutions and attributable to the action of the solvent upon the active molecules, may be represented by :

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* Ztschr. anal. Chem., 28, p. 203–218, from Ber. d. chem. Ges. **21**, p. **191**.

† Owing to the importance and general usefulness of this branch of analytical chemistry, this paper, which tends to systematize the methods and introduce correct formulas for calculating poloristrobometric analyses is given almost complete. J. F. G.

1. The percentage-content of inactive solvent

$$[\alpha] = A + Bq + Cq^2 \qquad (2).$$

2. The percentage content of active substance

$$[\alpha] = a + bp + cp^2 \qquad (3).$$

3. The concentration

$$[\alpha] = \mathfrak{A} + \mathfrak{B}c + \mathfrak{C}c^2 \qquad (4).$$

If the constants of the equations (2) and (3), determined by the examination of a number of solutions, are to be transposed, we have

$$\begin{array}{l|l} a = A + 100B + 10000C & A = a + 100b + 10000c \\ b = -B - 200C & B = -b - 200c \\ c = C & C = c \qquad (5). \end{array}$$

Formula (3) may be used for calculating the concentration and (4) for percentage-content when the sp. gr. of the solution is known, and by using $p = \frac{c}{d}$ or $c = pd$.

If for an active substance whose molecular weight is M, the constants in the equation (3) have been determined by trial, and these latter are to be calculated so as to represent one derivative affected by the molecular weight M_1, and whose formula shall be $[a]_1 = a_1 + bp + c_1 p^2$, then all the quantities of equation (3) must be multiplied by the factor $\frac{M}{M_1}$ whence for the new constants

$$a_1 = a \frac{M}{M_1} \quad b_1 = b \left(\frac{M}{M_1}\right)^2 \quad c_1 = c \left(\frac{M}{M_1}\right)^3. \qquad (6).$$

For changing Ventzke's saccharimeter degrees into angular degrees for the ray (D) the ratio is usually taken as

1° Ventzke = 0.3455 degrees (sodium light).

This ratio varies, however, for different substances, so that when accuracy is required, the factor should be determined by comparisons with the respective instruments. Thus

1° Ventzke (Gas light) =

Cane sugar	0.3465 ± 0.0005	degrees	(Na flame).
Milk sugar	0.3452 ± 0.0002	"	"
Grape sugar	0.3448 ± 0.0008	"	"
Invert sugar	0.3432 ± 0.0007	"	"
Cholesterin	0.3416 ± 0.0012	"	"
Turpentine	0.3494 ± 0.0009	"	"

The values are, moreover, affected somewhat by the degree of concentration.

The values for the concentration will be affected somewhat by the value of the unit volume—*i.e.* the true c. c., or Mohr's c. c. In most of the scientific determinations of the specific rotatory power of optically active substances the true c. c. was used, *i.e.* the 100 c. c. mark on the flasks indicates the volume of 99.72g of water at 20°; the solutions were weighed out at 20°, and the specific gravities were determined at the same temperature based upon water at 4°. For saccharimetric work 100 c. c. flasks have come into use, which were prepared according to the directions of Mohr, accordingly the 100 c. c. mark indicates the volume of 100g of water at 17.5°. The latter volume is used in the preparation of the normal sugar (26.048g) solution, which on the Ventzke scale causes a deviation of 100°*. Hence Mohr's c. c. (17.5°) ÷ 0.9977 will give the value for true c. c. at 20°. The sp. rot. powers determined with Mohr's concentration $\left(\mathrm{pd}\,\frac{17.5}{17.5}\right)$ would have to be multiplied by 0.9977 if the true c. c. is to be used as the unit volume.

Of the many compositions of which a solution may consist, the following shall be considered.

I.

Solutions, which consist of but one active substance and an inactive solvent.

The conditions here resolve themselves into two, according to

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* At least for the instruments manufactured by Schmidt & Haensch in Berlin.

the greater or less degree to which the sp. rot. power is affected by the concentration.

A. If the determinations show that the sp. rot. power of the substance is permanent, *i. e.* proportional to the concentration, then the quantity (c or p) in an unknown solution is found by the equation

$$c=\frac{100a}{[a]l} \qquad P=\frac{100a}{[a]ld} \qquad (7).$$

The same formula may be used for substances in which the variations due to concentration are but slight, by substituting an average result for $[a]$. The method may accordingly be used for the following substances .

1. Cane Sugar.—The well known method for determining cane sugar by means of the polariscope, or special saccharimeters, is based on the supposition that the ratio between rotation and concentration is uniform. The investigations of Schmitz and Tollens show, however, that the value of $[a]$ decreases as the concentration increases. Up to a concentration of $C=30$ the variation may be shown by the formulas

$$[a]_D^{20^\circ}=66.67-0.0095.\left(\text{True c. c. d}\frac{20}{4}\right)$$

$$[a]_D^{20}=66.82-0.0096.\,c.\left(\text{Mohr's c. c. d}\frac{17.5}{17.5}\right)$$

Whence for

c. =	5	10	15	20	25	30
True c. c. $[a]$=	66.62	66.58	66.53	66.48	66.43	66.38
Mohr's c. c. $[a]$=	66.78	66.73	66.68	66.63	66.58	66.54

If an average factor is taken as

$$[a]_D^{20}=66.5 \text{ for true c. c., } [a]_D^{20}=66.65 \text{ for M. c. c.}$$

then the concentration may be found from the observed angular rotation by the formulas

$$c=1.5038\frac{a}{l}\text{ for t. c. c., } c=1.5004\frac{a}{l}\text{ for M. c. c.}$$

giving for the extreme percentage-content of 5 and 30g variations of respectively +0.01 and −0.05 from the true result.

If the variations are to be taken into account then the formula of Schmitz*

$$c = 0.75063\,a + 0.0000766\,a^2 \text{ (true c.c.)}$$

may be used, in which a is the angular rotation observed in a 2 dm. column.

2. Milk Sugar.—Schmöger† found the specific rotatory power of solutions of milk sugar uniform up to a percentage-content of 36 ($c = 41.5$) and gives for the hydrate $C_{12}H_{22}O_{11} + H_2O$ the value

$$[a]_D^{20} = 52.53° \left(\text{t. c. c. d } \frac{20}{4}\right).$$

The rotation decreases as the temperature rises, and at about 20° the above value is increased or diminished 0.075 for each 1° temp.

The birotation which crystallized milk sugar shows shortly after solution can be changed to the constant by warming the solution. But if sugar dried at 100° is dissolved in cold water, the solution shows at first a lower rotation than the normal, which latter it attains after several hours on standing at ordinary temperatures or immediately after heating. Schmöger,‡ Erdmann.‖

3. Maltose.—$C_{12}H_{22}O_{11} + H_2O$. Dextro-rotatory. Meissl§ gives for the dependence of the sp. rot. power upon the %-content of the water solutions and the temperature of the same the formula

$$[a]_D^t = 140.375 - 0.01837.\ p - 0.095\ t \left(\text{t. c. c. d}^{\frac{17.5}{4}}\right)$$

which is true for variations of $p = 5$ to 35 and $t = 15$ to 35°.

Owing to the relatively small variation, by inserting an average factor

$$[a]_D^{17.5} = 138.3 \text{ or } [a]_D^{20} = 138.1$$

in formula (7) the error, even when $p = 30$, would be within hundredths %.

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*Ztschr. d.V. f. d. Rübenzucker-Ind. d. D. R. 1879, 950.

† Ber. d. chem. Ges., 1880, 885.

‡ Berr. d. chem. Ges., 1880, 1915, 2130.

‖ " " " " 1880, 2180.

§ Jour. f. Prakt. Chem. (II.), **25**, 114.

4. Raffinose (Melitose).—$C_{18}H_{32}O_{16}+5H_2O$.

Dextro-rotatory.—The specific rotary power for water solutions were found by:

a. Scheibler, by means of a quartz-wedge-saccharimeter

$$[\alpha]^{17.5}_{D} = 103.9 \text{ to } 104.0 \text{ for } c = 5 \text{ to } 16.$$

b. Tollens, by means of a half shadow instrument and Na. light,

$$[\alpha]^{20}_{D} = 104.44 \text{ to } 104.0 \text{ for } c = 10.$$

c. Rieschbiet and Tollens,*

$$[\alpha]^{20}_{D} = 102.41 - 104.9 \text{ for } c = 10.$$

d. von Lippmann $[\alpha]$ D $= 104.96$ for $p = 2.67$.

e. Finally Tollens† calculates from the data of Losseau $[\alpha]$ D $=$ 105.7, and of von Ritthausen $[\alpha]$ D $= 104.0$.

From which it appears that the sp. rotation is affected but little by the concentration, and that an average factor

$$[\alpha]^{20}_{D} = 104.5 \text{ may be used.}$$

In alcohol of 75% raffinose shows, according to Scheibler, the same rotatory power as in water.

Dextrose.—For the variations in sp. rot. power of dextrose solutions due to the %-content of the solutions, Tollens supplied the formula

$$[\alpha]\frac{20}{D} = 52.50 + 0.0188.p + 0.00052.p^2 \left(\text{t. c. c. d } \frac{20}{4}\right)$$

$$\text{whence for } \begin{matrix} p = 5 \\ [\alpha] = 52.61 \end{matrix} \quad \text{etc.} \quad \begin{matrix} p = 30 \\ [a] = 53.53 \end{matrix}$$

For solutions containing not over 20 g. in 100 c. c., the factor $[\alpha]\ \frac{20}{D} = 53.0$ is satisfactory.

For greater concentrations more accurate results are obtained by the author's new formula, $p = 0.948.\alpha - 0.0032.\alpha^2$, in which α is the angular rotation observed in a 2 dm. column.

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* Ann. Chem. (Liebig) **232**, 169. Z. V. J. R. I., 1886, 214.

† Ann. Chem. (Liebig) **232**, 170.

The birotation of a fresh solution of dextrose is destroyed by heating, or by letting the solution stand for twenty-four hours.

6. Lævulose. — The lævo-rotation of the aqueous solutions increases with the degree of concentration and diminishes as the temperature rises. The only reliable data are those of Herzfeld[*] and Winter[†] who used lævulose derived from inulin.

From these data it follows that the dependence of the sp. rotation at 20° temp. upon the %-content is expressed by

$$[\alpha]\frac{20}{D} = 69.53 - 0.0935 . p \left(\text{t. c. c. d } \frac{20}{4}\right)$$

$$\text{whence for } p = 5 \quad - \quad - \quad - \quad 30$$

$$[\alpha]\frac{20}{D} = -70.00 \quad - \quad - \quad - \quad -72.34$$

According to Herzfeld[‡], between the temp. of 20°—40° for each increase of 1° temp., the value of $[\alpha]\frac{20}{D}$ is lowered 0.5° for %-content of 10 to 40.

According to Winter,[§] lævulose dissolved in absolute alcohol, possesses a much lower sp. rot. power, namely,

$$[\alpha]\frac{20}{D} = -47.0 \text{ for } p = 7.78.$$

7. Invert Sugar.—The sp. rot. power of invert sugar obtained from cane sugar by the action of dilute acids, shows considerable variations, subject to the conditions of

(a.) The concentration.—Gubbe[**] found that for aqueous solutions of invert sugar, prepared by heating cane sugar solutions (containing 1 part of oxalic acid for every 100 parts invert sugar) for several hours at 60°, the sp. rot. p. at the temp. of 20° depended upon the %-content of water, as follows :

$$[\alpha]\frac{20}{D} = -23.305 + 0.01648, q + 0.000221, q^2 \left(\text{t. c. c. d } \frac{20}{4}\right)$$

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[*] Z. V. *f*. R. Z. I., 1884, p. 445, and 1886, p. 114.

[†] Loc. cit., 1887, p. 797.

[‡] Z. V. R. Z. I., 1884, p. 444.

[§] Z. V. R. Z. I., 1887, p. 807.

[**] Ber. d. chem. Ges., 1885, p. 2207.
Z. V. R. Z. I. 1884, p. 1345.

which for p. gives the formula

$$[\alpha]\frac{20}{D} = 19.447 - 0.06068,\ p + 0.000221.\ p^2.$$

This formula holds good for %-content up to p = 68.

For weaker solutions Gubbe gives for the concentration c the formula

$$[\alpha]\frac{20}{D} = -19.657 - 0.0361.c \left(t.\ c.\ c.\ d\,\frac{20}{4}\right)$$

which is true for c up to 35.

(b.) According to Tuchschmid the sp. rot. power diminishes 0.32 for each rise of 1° temp. between the temp. of 5° to 35°, when c = 17.21.

Gubbe gives the more accurate formulas :

$$t = 0^\circ \text{ to } 30^\circ$$

$$[\alpha]\frac{t}{D} = [\alpha]\frac{20}{D} + 0.3041\ (t-20) + 0.00165\ (t-20)^2$$

$$t = 20 \text{ to } 100^\circ$$

$$[\alpha]\frac{t}{D} = [\alpha]\frac{20}{D} + 0.3246\ (t-20) - 0.00021\ (-20)^2$$

(c.) The kind and quantity of acid used for the immersion, as well as the quantity of acid remaining in the solution. Gubbe found that oxalic acid did not affect the rotatory power, but hydrochloric and sulphurid acid increased it. The increased rotation in 9 per cent. solutions of invert sugar amounted to 0.362 per 1 g. hydrochloric acid, and 0.170 per 1 g. of sulphuric acid present.

For increased concentrations these variations are much diminished.

(d.) The time and degree of heat used during the inversion.

In Clerget's method the cane sugar solutions, to which are added 5% by sol. of concentrated hydrochloric acid (sp. gr. 1.88=38%), are heated for fifteen minutes at 67–70° and then rapidly cooled, Creydt*. If heated longer or at a higher temperature, the rotation may be diminished on account of decomposition.

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* Z. V. R. Z. I., 1887, p. 158.

(e.) The sp. rot. power of invert sugar is changed when acid-free solutions of invert sugar are evaporated in a vacuum to a syrupy consistency, probably owing to the formation of hydrated products (dextro-rotatory lævulosan?). On resolution dextro-rotation may be obtained, or at least a lævo rotation less than the normal. The latter may be reobtained by adding hydrochloric acid and setting the solution aside for several hours, or by heating for a short time at 67–70°

(g.) Further, the rot. power of invert sugar solutions is affected by the presence of other substances such as alcohol, acetate of lead, or lime.

8. Galaktose (Lactose). Dextro-rotatory.—Meissl found that the specific rotatory power of aqueous solutions of lactose as affected by %-content and temperature, is expressed by

$$[\alpha]\frac{\mathrm{t}}{\mathrm{D}} = 83.883 + 0.0785\,\mathrm{p} - 0.209\,\mathrm{t}\left(\mathrm{t.\ c.\ c.\ d}\,\frac{17.5}{4}\right)$$

which equation is good for

$$\mathrm{p} = 5 \text{ to } 35, \text{ and } = 10^\circ \text{ to } 30^\circ$$

Rindell gives

$$[\alpha]\frac{\mathrm{t}}{\mathrm{D}} = 83.037 + 0.199.\mathrm{p} - (0.276 - 0.0025.\mathrm{p})\left(\frac{\mathrm{n.\ c.\ c.}^2}{\mathrm{t}}\right)$$

when $\mathrm{p} = 11$ to 20, and $\mathrm{t} = 4^\circ$ to 40°. This would yield a value of 81.25 when $\mathrm{p} = 15$ and $\mathrm{t} = 20$, whereas the formula of Meissl gives 80.88, or 81.07 when based on Mohr's c. c. Fresh aqueous solutions of lactose show birotation, but after standing about six hours the normal rototion is obtained.

B. When the sp. rot. power of a substance is dependent upon the concentration to such a degree that the simple formula

$$\mathrm{c} = \frac{100\alpha}{[\alpha]\,\mathrm{l}}$$

can not be used, another form of calculation is adopted. In all such cases where the variation in sp. r. power can be expressed by a linear function and the third term of the equations (3) and (4) does not appear, the %-content of a solution may be found by

$$\mathrm{a} + \mathrm{b\,p} = \frac{100\alpha}{\mathrm{l\,d\,p}} \text{ or } \mathfrak{A} + \mathfrak{B}\mathrm{c} = \frac{100\alpha}{\mathrm{l\,c}},$$

whence
$$p = -\frac{a}{2\,b} \pm \sqrt{\left(\frac{a}{2\,b}\right)^2 + \frac{100}{b} : \frac{\alpha}{l\,d}}, \qquad (8a)$$

$$c = -\frac{\mathfrak{A}}{2\,\mathfrak{B}} \pm \sqrt{\left(\frac{\mathfrak{A}}{2\,\mathfrak{B}}\right)^2 + \frac{100}{\mathfrak{B}} \cdot \frac{\alpha}{l}}. \qquad (8\ b)$$

These formulas need be used only when only the formulas (3) and (4) are given for the active substance. If the data of the determination are at one's disposal, it is simpler to deduct the con stants of the equation of the form

$$p = a_1 \frac{\alpha}{l} + b_1 \left(\frac{\alpha}{l}\right)^2. \qquad (9\ a)$$

$$c = \mathfrak{A}, \frac{\alpha}{l} + \mathfrak{B}_1 \left(\frac{\alpha}{l}\right)^2 \qquad (9\ b),$$

hence taking p and c direct as functions of the angular rotation. These latter equations are also applicable when the variation of the sp. rot. power are represented by a curve, and hence equations (3) and (4) appear with all three members.

For example, a number of mixtures of nicotin and alcohol are given, the rotatory power of which had been determined by the author. The rapidly diminishing rotatory power as the % of alcohol q increased is expressed by the formula

$$[\alpha]\frac{20}{D} = -160.83 + 0.2224\ q,$$

which transposed for p, the value of nicotin, gives

$$[\alpha]\,\frac{20}{D} = -138.59 - 0.2224.\ p\left(t.\ c.\ c.\ d\ \frac{20}{4}\right),$$

and by inserting the constants of the equation (8 a)

$$p = +311.58 - \sqrt{97082.5 - 449.64\,\frac{\alpha}{l\,d}}$$

By use of formula (9 b), based upon calculations and experiments*, the following formula results

$$c = 0.704\,\frac{\alpha}{l} - 0.000525\left(\frac{\alpha}{l}\right)^2.$$

With these formulas very accurate determinations of nicotin

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* Ann. Chem., (Liebig) **189**, p. 320.

can be made, which suggests their use for determining the quantity of nicotin in tobacco.

In like manner the quantity of camphor in alcoholic solution may be determined.

According to the author's experiments* the rapid increase of the sp. rot. power as the concentration increases is expressed by the formula

$$[\alpha]\frac{20}{\mathrm{D}} = 41.982 + 0.11824.\ c\left(\text{t. c. c. d}\,\frac{20}{4}\right)$$

whence with formula (8 b) as a basis the following results,

$$c = -177.53 + \sqrt{31516.45 + 845.74\,\frac{\alpha}{l}}. \quad \text{(I.)}$$

From direct observations for the constants of equations (9 b) results

$$c = 2.3614\,\frac{\alpha}{l} - 0{,}01158\left(\frac{\alpha}{l}\right)^2 \quad \text{(II.)}$$

In the table supplied Z. A. C. **28**, p. 217, the results obtained by the use of the formulas are shown to be subject to an error of but — .16 to + 0.13 as extremes.

Instead of the above method another may be adopted for the calculation by first inserting in

$$c = \frac{100\alpha}{[\alpha]l}$$

an approximate value for $[\alpha]$ and recalculate with the value of c, obtained from $[\alpha] = \mathfrak{A} + \mathfrak{B}c$, the value $[\alpha]$. The latter result is then inserted in the first formula and the recalculations repeated 4 or 5 times until c becomes a constant quantity.

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* Ann. Chem., (Liebig) **189**, p. 333.

(TO BE CONTINUED.)