217. *The Properties of Nicotine and its Derivatives. Part IV. Refractive Dispersion. Part V. Magnetic Rotatory Dispersion.*

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PART IV. REFRACTIVE DISPERSION.

MEASUREMENTS of the refractive indices of nicotine were made by Gifford by the hollow-prism method (Gifford and Lowry, *Proc. Roy. Soc.*, 1927, *A*, 114, 592). This method is very accurate, but the scope of the work was limited by the strong absorption of light by

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* The compositions of the two ammine hydrates formulated are shown by the larger circles in Figs. 1 and 2, the circles marked A representing André's formula, $ZnSO_4,2NH_3,3H_2O$, and those marked B giving the correct composition corresponding with the formula $ZnSO_4,4NH_3,2H_2O$.

the thick column of liquid in the prism. The observations were therefore confined to a range of wave-lengths in the visible spectrum between 7685 and 4341 Å.U., although the absorption of the liquid does not become important before 3000 Å.U. in the ultra-violet. Since the refractive dispersion is most interesting in the immediate neighbourhood of the absorption band, it was thought advisable to make a further series of measurements in the ultra-violet, by the interferometric method which we have recently developed (*Proc. Roy. Soc.*, 1929, *A*, **126**, 165; 1931, *A*, **133**, 26) for measuring the refractive indices of thin films of liquid. Under these more favourable conditions the measurements have been extended to 2864 Å.U., *i.e.*, within 200 Å.U. from the head of an absorption band, with a maximum molecular extinction coefficient $\log \varepsilon = 3{\cdot}43$ at 2650 Å.U. in *cyclo*hexane.* Measurements were also made, with an improved Pulfrich refractometer, of the refractive indices for 28 wave-lengths in the visible spectrum. These are less exact than Gifford's measurements, since they are only valid to the fourth decimal; but they are probably more trustworthy, by reason of a closer control of temperature and more recent purification of the material.

Throughout the tables, $(O - C)$ represents the difference between the observed and the calculated value.

The data thus obtained are set out in Table I. They have been analysed by the methods already used in the more difficult case of benzene (Lowry and Allsopp, *loc. cit.*). The refractive dispersion is approximately simple in the visible spectrum, where it is controlled almost entirely by a single absorption band; but its real complexity is revealed by the ultra-violet data. The refractive indices can, however, be represented throughout the whole range λ 6708—2864 Å.U. by a Ketteler–Helmholtz expression with six constants, namely:

$$n^2 = 1{\cdot}22577 + \frac{1{\cdot}006153\,\lambda^2}{\lambda^2 - 0{\cdot}0173626} + \frac{0{\cdot}03983\,\lambda^2\,(\lambda^2 - 0{\cdot}0668950)}{(\lambda^2 - 0{\cdot}0668950)^2 + 0{\cdot}00006931\,\lambda^2}$$

The two variable terms in this equation represent the influence of characteristic frequencies in the distant Schumann region at $\lambda = 1326$ Å.U., and in the middle ultra-violet at $\lambda = 2586$ Å.U. In the visible spectrum, the low-frequency term is about 100 times smaller than the high-frequency term; the damping factor in this term only becomes important within the region in which the absorption due to the band is already very marked.

The divergences of the observed values from those calculated from this equation are shown in the last columns of Table I. The

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* In Part III (J., 1931, 320) the maxima of absorption by methylnicotone in water and in *cyclo*hexane are shown correctly in Fig. 2 but have been interchanged in the text.

TABLE I.

Refractive Indices of Nicotine at 20°.

First Series: Pulfrich Refractometer Readings.

λ, Å.U.	*n*.	Diff., (*O* − *C*) × 10^4.	λ, Å.U.	*n*.	Diff., (*O* − *C*) × 10^4.
Li 6707·86	1·5229	+1	Ag 5209·04	1·5341	±
He 6678·15	1·5231	−1	Cu 5153·26	1·5346	−2
Hα 6562·85	1·5235	−1	Cu 5105·55	1·5353	±
Cd 6438·47	1·5241	−2	Cd 5085·82	1·5354	±
Zn 6362·34	1·5244	−3	He 5015·68	1·5367	+2
Li 6103·6	1·5262	−1	Ba 4934·10	1·5375	±
Na 5895·93	1·5278	±	Hβ 4861·33	1·5386	+1
He 5875·62	1·5279	±	Cd 4799·91	1·5395	±
Hg 5790·66	1·5285	−1	Zn 4722·16	1·5408	+2
Cu 5782·15	1·5287	+1	Zn 4680·14	1·5414	+1
Cu 5700·24	1·5294	+1	Cd 4678·15	1·5414	+1
Ag 5471·51	1·5312	−2	Li 4603·0	1·5426	−1
Hg 5460·73	1·5313	−2	He 4471·48	1·5455	+3
Cu 5220·06	1·5339	−1	Hg 4358·34	1·5476	+1

Second Series: Photographic Readings.

λ, Å.U.	Film.*	*n*.	Diff., (*O* − *C*) × 10^4.	λ, Å.U.	Film.*	*n*.	Diff., (*O* − *C*) × 10^4.
W 4680·539	*b*	1·5413	−2	Fe 3545·642	*b*	1·5744	±
Fe 4484·238	*b*	1·5449	−1	Fe 3468·849	*a*	1·5784	±
W 4436·912	*b*	1·5457	−2	Fe 3465·864	*b*	1·5788	+3
Fe 4415·126	*b*	1·5465	±	Fe 3415·537	*b*	1·5820	+5
W 4378·501	*a*	1·5468	−4	Fe 3378·682	*b*	1·5844	+6
Fe 4325·764	*b*	1·5483	±	W 3354·451	*b*	1·5859	+5
Fe 4282·406	*b*	1·5491	−1	Fe 3307·238	*b*	1·5888	+2
Fe 4260·489	*b*	1·5494	−3	Fe 3284·597	*b*	1·5905	+1
W 4244·374	*a*	1·5502	+1	Fe 3280·268	*a*	1·5908	+1
Fe 4219·364	*b*	1·5506	±	Fe 3246·015	*a*	1·5937	+3
Fe 4199·098	*b*	1·5512	+1	Fe 3230·976	*b*	1·5955	+8
Fe 4157·805	*b*	1·5518	−4	Fe 3219·817	*b*	1·5962	+5
Fe 4118·549	*b*	1·5529	−3	Fe 3209·328	*b*	1·5971	+6
W 4099·029	*b*	1·5535	−2	W 3198·843	*b*	1·5981	+7
Fe 4005·246	*b*	1·5562	−2	Fe 3188·837	*b*	1·5991	+7
Fe 3932·631	*b*	1·5581	−5	Fe 3180·220	*a*	1·5994	+3
Fe 3888·518	*a*	1·5599	−1	Fe 3178·545	*b*	1·6000	+7
W 3881·402	*b*	1·5601	±	Fe 3157·877	*b*	1·6017	+4
W 3864·108	*b*	1·5606	−2	W 3127·344	*b*	1·6042	−2
Fe 3846·805	*b*	1·5613	−1	W 3117·580	*b*	1·6052	−2
Fe 3836·339	*a*	1·5619	±	Fe 3099·898	*b*	1·6075	±
Fe 3798·514	*b*	1·5631	−1	W 3089·321	*a*	1·6088	+2
Fe 3765·544	*b*	1·5640	−1	W 3080·431	*b*	1·6097	±
Fe 3734·869	*a*	1·5653	−4	W 3062·601	*b*	1·6120	+1
Fe 3704·464	*b*	1·5670	+1	Fe 3045·082	*b*	1·6144	+2
Fe 3687·440	*a*	1·5675	−1	Fe 3031·216	*a*	1·6152	−2
Fe 3659·521	*b*	1·5690	+1	Fe 3018·988	*b*	1·6179	+1
W 3640·144	*a*	1·5696	−3	Fe 3003·034	*b*	1·6205	+4
Fe 3630·353	*b*	1·5704	+3	W 2979·860	*a*	1·6235	−1
Fe 3586·989	*b*	1·5722	±	Fe 2953·943	*a*	1·6271	−6
Fe 3573·894	*b*	1·5733	+5	Fe 2863·866	*a*	1·6475	−2
Fe 3559·514	*b*	1·5738	+2				

* See p. 1616.

mean deviation for 28 wave-lengths in the visible spectrum is ± 0·0001 and the mean error − 0·00001. The corresponding numbers for 63 photographic readings are ± 0·00024 and + 0·00006 respectively. For the whole range of 91 wave-lengths, λ 2863 to 6708 Å.U., the mean deviation is ± 0·00020 and the mean error only + 0·00004.

Materials and Methods of Measurement.—The methods of measurement have already been described (*loc. cit.*). The sample of nicotine, purified through the zinc chloride compound by the method of Ratz (*Monatsh.*, 1905, **26**, 1241), had already been used for the measurements of absorption and rotatory dispersion which are described in Parts I and II of this series of papers (*Proc. Roy. Soc.*, 1931, *A*, **133**, 26, 36). It was redistilled under reduced pressure in a current of hydrogen until colourless, and was distilled again immediately before use. The remarkable solvent power of the liquid made it difficult to handle, but Ash's " Sylca " (dental) cement was found to be sufficiently resistant for use in fixing the glass cell to the prism of the refractometer. Oxidation, which takes place very rapidly when nicotine is exposed to air, was prevented by covering the cell with a small hood through which a stream of dried nitrogen was directed on to the surface of the liquid. Control experiments suggested that the absorption of atmospheric moisture might be a more serious factor than oxidation, and it was therefore found advisable to renew the material in the cell from time to time, and to watch for changes of composition by making frequent readings of the " angle of emergence " of a standard line (He 5876).

These difficulties were not encountered when making photographic readings of refraction in the ultra-violet with the étalon refractometer. Two or three drops of liquid sufficed to make the film, and these films were found to be particularly stable and easy to manipulate as a result of the low volatility of the liquid. Moreover, oxidation and absorption of moisture were reduced to a minimum by reason of the fact that the longest exposure required to provide data for a complete series of ultra-violet readings was about 4 minutes. The thicknesses of the two films employed for this purpose were $a = 8{\cdot}35\,\mu$, and $b = 30{\cdot}7\,\mu$; the former was transparent as far as 2787 Å.U., although the interference fringes could not be read below 2864 Å.U.

Comparison with Previous Observations.—In addition to the measurements made by Gifford, the refractive dispersion of nicotine was recorded by Brühl (*Z. physikal. Chem.*, 1895, **16**, 193) for six wave-lengths between Li 6708 and Hγ 4341 at 18·8°. After correction to 20° by means of the temperature coefficients given by Gifford, the values are uniformly 0·0004 higher than those now recorded. On the other hand, Gifford's values at 15° for 13 wave-lengths between $\lambda = 7865$ and $\lambda = 4341$, when corrected in the same way, are on the average 0·0003 lower than the new measurements. Gifford's sample was supplied from Cambridge, and was initially identical with that employed for the present series of investigations. When used, it had not yet developed any yellow colour by oxidation, in spite of the restricted range of wave-lengths which were transmitted through it; but it may have absorbed moisture during the course of the measurements, since great difficulty was experienced in retaining it inside the hollow prism. In view of the initial purity of the material, and the precautions taken to avoid contamination during the present series of readings, we believe that the refractive indices now recorded (which lie uniformly between those given by the two previous observers) are the most trustworthy yet obtained.

PART V. MAGNETIC ROTATORY DISPERSION.

The magnetic rotatory dispersion of nicotine was measured with the same magnet and by the same methods (Lowry, J., 1913, **103**, 1322) as those of a long series of aliphatic compounds which had been examined by one of us (Lowry, J., 1914, **105**, 81). Readings were made for 12 wave-lengths in the visible spectrum.

In order to deduce the value of Verdet's constant from the observed rotations, the rotation produced by an equal column of water was read. The values of the constant for water at various wave-lengths have recently been measured very accurately by Roberts (*Phil. Mag.*, 1930, **9**, 361) so that the constants for nicotine can now be deduced by direct comparison with his readings for Hg 5461.

The results are set out in Table II, which shows (i) the double deflexion observed with a column 1 dm. long, after correction for the effect of the end-plates, (ii) the values of Verdet's constant deduced from these readings, and (iii) the ratio of the rotation at any wave-length to that at the wave-length of the green mercury line. The observed ratio $\delta_{4358}/\delta_{5461}$ is 1·664, which is appreciably higher than those of the saturated aliphatic compounds examined previously, but lower than for the unsaturated ones.

Correlation of the Optical Properties of Nicotine.—The optical properties of nicotine appear to be controlled by two characteristic frequencies. The first corresponds with the familiar absorption band in the middle ultra-violet, with a maximum $\log \varepsilon = 3{\cdot}43$ at 2640 Å.U. in *cyclo*hexane. This band is about 100 times more intense than that of camphor, so we have not been able to penetrate it either by measurements of refraction, as in the case of *cyclo*hexanone with $\log \varepsilon = 1{\cdot}12$ at 2880 Å.U., or by measurements of rotatory dispersion, as in the cases of camphor, $\log \varepsilon = 1{\cdot}35$ at 2900 Å.U., and of camphorquinone, $\log \varepsilon = 1{\cdot}53$ at 4750 Å.U.

TABLE II.

Magnetic Rotatory Power of Nicotine at 20°.

l = 10 cm.; double rotation, 2α, of water at 5461 Å.U. = 7·10°; Verdet's constant for water at 5461 Å.U. = 0·01534 min. per cm. gauss.

	λ, Å.U.	2α (corr.).	Verdet's constant, δ, min./cm. gauss.	δ/δ_{5461}.	δ/δ_{5461} calc. from equation (VI).	(VII).
Li	6707·86	7·60°	0·01643	0·593	0·642	0·643
Cd	6438·47	8·47	0·01831	0·661	0·699	0·701
Zn	6362·35	8·85	0·01911	0·690	0·717	0·719
Li	6103·6	9·72	0·02100	0·758	0·785	0·786
Na	5892·62*	10·53	0·02274	0·821	0·847	0·848
Hg	5780·13*	11·00	0·02379	0·859	0·883	0·884
Ag	5467·71*	12·79	0·02764	0·998	0·998	0·997
Hg	5460·73	12·82	0·02770	1·000	1·000	1·000
Ag	5209·04	14·21	0·03072	1·109	1·111	1·110
Cd	4799·91	17·09	0·03689	1·332	1·339	1·332
Li	4602·5*	18·67	0·04033	1·456	1·471	1·466
Hg	4358·34	21·34	0·04609	1·664	1·671	1·663

* Mean wave-lengths.

The values shown in the last two columns have been calculated from the formulæ of de Malleman (VI) and Becquerel (VII):

$$\text{(VI.)}\ \frac{\delta}{\delta_{5461}} = 0{\cdot}2525\,\frac{(n^2-1)^2}{n\lambda^2};\quad \text{(VII.)}\ \frac{\delta}{\delta_{5461}} = 0{\cdot}9457\,\frac{n^2(n^2-1)}{\lambda^2}$$

(Lowry and Gore, *Proc. Roy. Soc.*, 1932, *A*, **135**, 13). By exception, the characteristic frequencies deduced by extrapolation from measurements of rotatory dispersion, $\lambda_{\text{max.}} = 2450$, and from measurements of refractive dispersion $\lambda_{\text{max.}} = 2586$ Å.U., are for *shorter* wave-lengths than the directly-observed head of the band.

The second characteristic frequency is in the Schumann region at 1326 to 1740 Å.U. The position and magnitude of this second absorption band have not been observed directly, since it lies beyond the limit of transmission of light by air or by quartz; but, as usual, it appears to be far more intense than the bands which have been recorded in the more accessible part of the ultra-violet spectrum. Direct evidence of the existence of a second absorption band is provided by the development of a strong general absorption in all those derivatives of nicotine in which the *pyridyl* nitrogen is ionised, although it is not observed either in nicotine itself or in those derivatives in which only the *pyrrolidine* nitrogen is ionised. This general absorption may represent the foot of the intense band in the Schumann region; but alternatively it might be due to a third absorption band in an intermediate position near the edge of the Schumann region.

The relative influence of these two absorption bands varies very greatly in different optical properties and in different derivatives. The most remarkable fact is the dominance by the near ultra-violet band of the optical rotatory power of nicotine, which can be expressed very nearly by a single term of Drude's equation, with $\lambda_0 = 2450$ Å.U. (Lowry and Lloyd, J., 1929, 1771). This predominance persists in chloronicotine and in methylnicotine (Lowry and Gore, J., 1931, 319), where both nitrogen atoms are tervalent and neutral, as well as in nicotine *iso*methiodide (Lowry and Lloyd, J., 1929, 1779), where the *pyrrolidine* nitrogen remains neutral, although the *pyridyl* nitrogen is ionised by the addition of a methyl radical. When, however, the *pyrrolidine* nitrogen, which is attached directly to the asymmetric carbon atom, is ionised, *e.g.*, by converting the base either into a salt or into a methiodide, the influence of the ultra-violet absorption band disappears abruptly. The rotatory dispersion of this group of derivatives is then dominated by a characteristic frequency in the Schumann region at 1480—1740 Å.U., whilst the sign of the rotations is reversed. This change is not accompanied, however, by any *decrease* in the intensity of the band, which actually *increases* from log $\varepsilon = 3{\cdot}43$ in the lævorotatory base to about 3·8 in its dextrorotatory derivatives.

The refractive dispersion of nicotine, as recorded in Part IV (above), is probably controlled by the same absorption bands as the rotatory dispersion, but the influence of the Schumann band on the refractive indices in the visible spectrum is now 100 times greater than that of the ultra-violet band. It is therefore not surprising that we have been unable to find any support for de Malleman's suggestion (*Ann. Physique*, 1924, **2**, 1) that rotatory dispersion and refraction may be correlated by means of the expression

$$[M] = (n^2 - 1)^2(\mathrm{B}/\lambda^2)(1 - \lambda_0{}^2/\lambda^2)$$

where $[M]$ is the molecular rotation at wave-length λ, n the refractive index, λ_0 the wave-length of the characteristic frequency, and B a constant. Such a correlation is indeed unlikely to be realised in practice (as de Malleman himself found), since it depends on the hypothesis that the same electrons are equally concerned in both phenomena, whereas in fact one property is perfectly general, whilst the other is a highly specific property of dissymmetric molecules.

For similar reasons Wiedemann's law of proportionality between optical and magnetic rotatory powers breaks down completely in the case of nicotine, as it does in the majority of optically active liquids (Lowry, Pickard, and Kenyon, J., 1914, **105**, 94), although it is approximately true in the cases of quartz (Lowry, *Phil. Trans.*, 1912, *A*, **212**, 295) and of molten menthol (Salceanu, *Compt. rend.*, 1931, **192**, 1218).

Magnetic Rotation and Refraction.—A much closer correlation may be expected between refractive dispersion and magnetic rotatory

TABLE III.

Magnetic Rotatory Power of Nicotine.

Equations involving a dispersion constant.

$$\text{(I.)}\ \frac{\delta}{\delta_{5461}} = n\left[\frac{0{\cdot}2546}{\lambda^2 - 0{\cdot}01736} - \frac{0{\cdot}0673}{\lambda^2}\right] \qquad \text{(I}'\text{.)}\ \frac{\delta}{\delta_{5461}} = n\left[\frac{0{\cdot}1800}{\lambda^2 - 0{\cdot}02266}\right]$$

$$\text{(II.)}\ \frac{\delta}{\delta_{5461}} = \frac{1}{n}\left[\frac{0{\cdot}0166}{\lambda^2} + \frac{0{\cdot}3903\,\lambda^2}{(\lambda^2 - 0{\cdot}01736)^2}\right] \qquad \text{(II}'\text{.)}\ \frac{\delta}{\delta_{5461}} = \frac{1}{n}\left[\frac{0{\cdot}4066}{(\lambda^2 - 0{\cdot}01679)^2}\right]$$

$$\text{(IV.)}\ \frac{\delta}{\delta_{5461}} = \frac{0{\cdot}2711}{\lambda^2 - 0{\cdot}02708} \qquad \text{(V.)}\ \frac{\delta}{\delta_{5461}} = \frac{0{\cdot}5353\,(n-1)}{\lambda^2 - 0{\cdot}01380}$$

Wave-length, λ.		$\frac{\delta}{\delta_{5461}}$ obs.	$\frac{\delta}{\delta_{5461}}$ calc. from equation					
			(I).	(I′).	(II).	(II′).	(IV).	(V).
Li	6707·86	0·593	0·641	0·641	0·640	0·642	0·641	0·643
Cd	6438·47	0·661	0·699	0·699	0·699	0·699	0·699	0·700
Zn	6362·35	0·690	0·717	0·717	0·717	0·717	0·717	0·718
Li	6103·6	0·758	0·785	0·785	0·784	0·784	0·785	0·785
Na	5892·62	0·821	0·846	0·847	0·846	0·846	0·847	0·847
Hg	5780·13	0·859	0·883	0·882	0·884	0·883	0·883	0·883
Ag	5467·71	0·998	0·997	0·997	0·997	0·997	0·997	0·997
Hg	5460·73	1·000	1·000	1·000	1·000	1·000	1·000	1·000
Ag	5209·04	1·109	1·110	1·110	1·110	1·110	1·110	1·110
Cd	4799·91	1·332	1·336	1·336	1·336	1·336	1·336	1·333
Li	4602·5	1·456	1·469	1·469	1·469	1·469	1·469	1·467
Hg	4358·34	1·664	1·664	1·664	1·664	1·664	1·664	1·664

power, since it is probable that both of these phenomena are influenced by *all* the valency electrons in the molecule. On this basis, various classical and quantum investigations have produced formulæ relating the two quantities to one another. The earliest of these were deduced by Drude, who made use of two different fundamental concepts, and obtained for Verdet's constant the expressions :

$$\text{(I.)}\quad \delta = n\left(\frac{a}{\lambda^2} + \frac{b}{\lambda^2 - \lambda_0^2}\right) \qquad \text{(II.)}\ \delta = \frac{1}{n}\left(\frac{a}{\lambda^2} + \frac{b\,\lambda^2}{(\lambda^2 - \lambda_0^2)^2}\right)$$

In these formulæ, n is the refractive index at wave-length λ, a and b are constants, and λ_0 is the wave-length of the characteristic frequency in the Ketteler–Helmholtz equation for refractive dispersion. The second expression received brilliant confirmation through the work of R. W. Wood (*Phil. Mag.*, 1905, **10**, 408) on sodium vapour, which showed that the sign of the rotation was the same on opposite sides of the absorption band. In practice, the a/λ^2 term is negligibly small, and the expressions (I) and (II) reduce to :

$$\text{(I}'\text{.)}\ \delta = \frac{n\,b}{\lambda^2 - \lambda_0^2} \qquad \text{(II}'\text{.)}\ \delta = \frac{1}{n}\left[\frac{b\,\lambda^2}{(\lambda^2 - \lambda_0^2)^2}\right]$$

The expression

$$\text{(III.)}\ n\delta\lambda^2 = k[\lambda^2/(\lambda^2 - \lambda_0^2)]^2$$

deduced by Richardson (*ibid.*, 1916, **31**, 232, 454) and used recently by Evans (*ibid.*, 1927, **3**, 546, etc.) is obviously identical with the latter of these. Lowry, however (J., 1914, **105**, 81), expressed magnetic rotatory dispersion on a purely empirical basis by means of Drude's equation for optical rotatory dispersion, which does not involve refractive indices, *viz.*,

$$\text{(IV.)}\quad \delta = k/(\lambda^2 - \lambda_0^2).$$

In the derivation of these formulæ, no account was taken of molecular structure. An attempt to do this led J. J. Thomson (*Phil. Mag.*, 1920, **40**, 713) to the equation

$$\text{(V.)}\quad \delta = A(n - 1)/(\lambda^2 - \lambda_0^2).$$

By using a much more elaborate quantum theory of the phenomenon, de Malleman (*J. Physique*, 1926, **7**, 295) arrived at the equation

$$\text{(VI.)}\quad \delta = A(n^2 - 1)^2/n\lambda^2$$

where the constant A involves the molecular dimensions. Finally, Becquerel (*Ann. Chim.*, 1877, **12**, 5; 1880, **21**, 289) developed a remarkable empirical formula, whereby magnetic rotatory dispersion may be predicted from refractive dispersion by means of the relation

$$\text{(VII.)}\quad \delta = An^2(n^2 - 1)/\lambda^2.$$

These formulæ are of two types, since the magnetic rotatory dispersion may be represented either (i) by an equation involving an arbitrary dispersion constant, with or without the refractive index of the medium, or (ii) by an equation in which only the refractive index is used to express the influence of variations of wave-length on the magnetic rotation in the medium. In the former case the equations for magnetic rotatory dispersion contain *two* arbitrary constants, and the dispersion curves can be made to fit *two* experimental points. In the latter case, they contain only *one* arbitrary constant and the course of the dispersion curve is therefore determined completely when the rotation for *one* wave-length is given. Tables II and III show the results obtained by making use of 6 equations of the former type (of which 5 involve the refractive index) and two equations of the latter type. It is at once obvious from Table III that the equations which involve two or more arbitrary constants give calculated values which are substantially identical with one another, so that, when the rotations for the green and violet mercury lines are given, those for longer wave-lengths are almost independent of the formula selected. The experimental values for the red and yellow lines diverge somewhat widely, however, from the theoretical values, apparently because they depend on a more complex type of absorption.

The equations of de Malleman and of Becquerel (see Table II), which contain only one arbitrary constant, diverge progressively from one another. The divergence is not large on passing from green to red, where the dispersion ratio $\alpha_{6708}/\alpha_{5461}$ is almost constant at 0·642; but it is substantially greater in the direction of shorter wave-lengths, so that the ratio $\alpha_{4358}/\alpha_{5461}$ is 1·671 for de Malleman's formula and 1·663 for Becquerel's. The latter formula is in amazing agreement with the experimental ratio 1·664, in view of the fact that it is a pure prediction from measurements of a totally different optical property; but the divergence between the experimental and calculated values for the yellow and red lines still persists, and is apparently not capable of being removed by any simple process.

Summary.

(*a*) Values are given for the refractive indices of nicotine at 20° for 28 wave-lengths in the range of visual observations with a modified Pulfrich refractometer, and for 63 wave-lengths in the region covered by photographic readings with an étalon refractometer. The photographic readings extend to $\lambda = 2863$ Å.U., *i.e.*, within 200 Å.U. from the head of the characteristic absorption band.

(*b*) These refractive indices can be represented, with a mean deviation of ± 0·00020 and a mean error of + 0·00004, by the equation :

$$n^2 = 1{\cdot}22577 + \frac{1{\cdot}006153\,\lambda^2}{\lambda^2 - 0{\cdot}0173626} + \frac{0{\cdot}03983\,\lambda^2\,(\lambda^2 - 0{\cdot}0668950)}{(\lambda^2 - 0{\cdot}0668950)^2 + 0{\cdot}00006931\,\lambda^2}$$

The second term, with a characteristic frequency in the Schumann region at 1326 Å.U., is approximately 100 times greater in its effect in the visible spectrum than the third term, with a characteristic frequency in the middle ultra-violet at 2586 Å.U.

(*c*) Verdet's constants for the magnetic rotatory power of nicotine have been recorded for 12 wave-lengths in the visible spectrum. The relationship of magnetic rotatory power to other optical properties of nicotine is discussed.

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