On the Numerical Relation between the Index of Refraction and the Wave-length within a Refractive Medium, and on the Limit of Refraction

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series of papers, of which this formed one, was republished in book form at the end of the same year. This was before I had the honour of membership in the Physical Society, or doubtless I should have then brought the subject more immediately under your notice; but upon my being elected a member I lost no time in presenting a copy to this Society, and those who care to examine this question will find therein a chapter devoted to this very employment of the dynamometer to determine Coefficients of Self- and Mutual-Induction and the Capacity of Condensers.

March 1888.

XXIV. *On the Numerical Relation between the Index of Refraction and the Wave-length within a Refractive Medium, and on the Limit of Refraction.* By T. PELHAM DALE, M.A.*

THE following equation (see Sir Geo. Airy's Treatise on the Undulatory Theory, ed. 1877, p. 93) is proposed as expressing the relation between wave-length and velocity of propagation in an isotropic medium:—

$$v = \sqrt{\left(1 - \frac{1}{2^{\frac{3}{2}}}\right)^m} \cdot \frac{\sin \frac{\pi h}{\lambda}}{\frac{\pi h}{\lambda}} \dots \dots \dots (\alpha)$$

v is here the velocity of propagation, h the distance between the undulating particles, λ the wave-length, m the absolute force of attraction, supposed to follow the law of the inverse square.

For our purpose this may be put under the form

$$v = k \sin \frac{\pi h}{l} / \frac{\pi h}{l} \dots \dots \dots (\beta)$$

It is convenient to reserve λ to signify the wave-length in free æther, and to use l for the wave-length within the medium. The values of the wave-lengths in free æther are those given in the text-book of Glazebrook and the tables of Lupton.

Now, knowing the index of refraction for any fixed line by observation of the index μ , the corresponding value of l is given by the equation

$$l = \frac{\lambda}{\mu}.$$

* Read February 11, 1888.

observation of little consequence. In the case of the liquids examined I am altogether indebted to Dr. Gladstone, who furnished me with those contained in Table III. for the purposes of this investigation. When the line B is given, the octave ray to H may be obtained from A by interpolation, and these values were calculated by this method. It gives results sufficiently near the truth, but has been verified in case of CS_2 (temp. 10.5) and mint hydrocarbon by reference to the two indices A and H, so that the table depends on these two indices only.

It will be seen that in the cases examined $\frac{\nu-1}{d}$ is constant, within the limits of observation, unaffected by temperature.

Dr. Gladstone and myself, in our joint paper, read before the Royal Society, May 6, 1863, and printed, p. 317, in the Transactions, have pointed out that in consequence of an accidental relation amongst the coefficients used in Cauchy's series, that the equation

$$\nu = \mu_H - 3(\mu_F - \mu_B)$$

holds with considerable accuracy in the cases examined. It appears generally to give a fair approximation to the limit*, and thus to interpolate indices within the visible spectrum.

While, however, this investigation was in progress Prof. Langley's first paper on the determination of wave-lengths in the invisible spectrum appeared (Phil. Mag. March 1884). He there gives the wave-lengths of lower heat-rays down to length 2.030, and shows that the observed indices of refraction are not only below the limit obtained by Cauchy's formula, but even below those found by other formulæ. The material of his prism was flint glass. I found that the values derived from θ_H and θ_{2H} , while fairly accurate in the visible spectrum, were increasingly discordant in the longer wave-lengths. If θ_H were increased the lower indices were found more accordant; but then the visible spectrum was not adequately represented within the limits of any error which could be imagined possible. This seemed to throw a doubt on the existence of a limiting value. It appeared, however, that the glass prism absorbed the longer waves considerably. The

* The divergence in case of CS_2 is, however, considerable, and ν is too large in comparison with that given by the above equations. Especially does this occur in highly dispersive media.

Phil. Mag. for May 1886 contained another paper by Prof. Langley, the material of the prism being rock-salt. On comparing the values found by observation with those furnished by the above equations, the agreement was sufficiently close to encourage investigation, and, accordingly, the calculations were carried further, the approximation being to single seconds in the value of θ and every value found.

The results are embodied in Tables I. and II. It will be seen in the case of rock-salt that the agreement between the values obtained from the sine—which involve only wave-lengths in free æther—and those obtained from the arc, which involve the two indices, and which should be equal to the former, are very close. The errors, it will be observed, are of small amount and not of uniform sign, possibly, however, showing a small tendency to increase on the side of angle from the sine in the case of the lower indices. Turning to the table of indices in the case of flint glass, we see that the angle for H, $24^{\circ} 18' 40''$, gives fairly accordant values down to wave-length 0.940, and not far from the truth to 1.270; after this the values increase in the case of the sine over that of the arc, or, in other words, the calculated index comes out too large. This is the more important because the proportionate increase on so small an angle as 4° makes a large increase in the resulting index. If the value of θ_H be increased, this difference is diminished in the lower values; but it would require an increase far greater than could possibly be allowed as due to errors of observation in order to include the lower values, and the upper would become greatly discordant with observation.

It was, however, noticed by Prof. Langley that the flint-glass prism appeared strongly absorbent of the lower rays. It would no doubt be unsafe to reason very confidently from results obtained from only two substances. We may remark, however, that the approach to limit of refraction, if it exist, must display itself in observation by a small increase in the index for a large proportionate increase in the wave-length. Any disturbing cause then must become, proportionately, also increasingly effective as the wave-length increases. Hence must arise a tendency to mask the limiting value if attempted to be found by observation. Now in the case of

flint glass we can hardly suppose but that some effect is produced by the change of temperature which results from the passage of the heat-rays through the medium. In the case of fluids the heat lowers the index, and thus the limit would be lowered also, and in somewhat greater proportion. It is, in the absence of sufficient data, not easy to say what would be the effect of this change of temperature in solids. In the case of glass, the *course* of the ray through the medium would possibly be raised in temperature above the surrounding mass; and thus there would be a cylinder of glass through which the pencil of rays passed, which might be in a state of constraint as compared with that around it. That a state of constraint exists is shown by the glass "flying" when suddenly heated.

However this may be, it seemed desirable in the first place to continue the investigation with the data at hand, and to calculate the value of the limit as given by the above equations, using as data two observed indices only. The results are given in the tables, and will be seen to include a considerable number of fluids differing widely in specific gravity, optical properties, and chemical constitution. The list it will be noticed includes certain isomeric bodies and also several differing by a single component.

The first fluid examined was bisulphide of carbon at different temperatures, the data for which were furnished by Dr. Gladstone to me for the purpose of this investigation. It will be seen that the quantity $\frac{\nu-1}{d}$ is practically a constant.

The same result is observable in the case of mint hydrocarbon and benzene. The range of temperature is not indeed very large, but within the limits taken it is evident that the specific gravity and the quantity $\nu-1$ increase or diminish *pari passu*, and there is but little doubt that this relationship obtains generally. It would be very desirable indeed to have longer ranges of temperature* if these could be procured without corresponding errors which high temperature would almost certainly have a tendency to introduce.

* This is especially desirable near boiling and freezing points. It is possible that the specific gravity at boiling-point might reveal relations at present masked by the arbitrary character of specific gravities taken at any temperature convenient for observation.

It is of interest evidently, in the case of a highly dispersive substance, to determine how far the different indices yield the same limit, as they clearly should do if the formulæ are exact. For the determination of this a value of θ was chosen which should yield the value which would satisfy θ_A ; and then wave-lengths of lines B C D E F and G in free æther and in the medium were treated so as to find θ_B &c. If the sine and arc give the same result, then calculation and observation agree. It will be seen that in the case of CS_2 there is an outstanding difference which amounts to not quite three minutes of arc, and increases from A to H. This is equivalent to saying that the formulæ give correct results to the third place in the case of CS_2 . This is not so good as the rock-salt in Table II. The index of G is most affected. The difference was noticed by the late Professor Baden Powell, in his 'Undulatory Theory as applied to the Dispersion of Light,' London, 1841. This matter deserves further investigation, but it is a matter also which will involve a considerable amount of calculation; thus it seemed right to postpone this for the present, as being better policy to obtain first a sufficient number of values of ν in case of media varying considerably in optical properties.

It seemed also desirable to include in the choice of bodies several which were isomeric. There is a certain analogy in these to a body at different temperatures, as in either case we are dealing with the same chemical elements. The result is, as will be seen from examining the tables, that in many cases $\frac{\nu-1}{d}$ is very nearly a constant. In no case yet examined is the divergence very great. Thus in benzene and styrolene, cresol, metacresol, and benzil alcohol, benzil chloride and chlorotoluine, methyl citraconate and methyl mesaconate, the agreement is close; but in case of picoline and aniline, as also acetone—with which butyric ether agrees—as compared with allyl alcohol there is a difference of about three units in the second place*. It may be merely an accidental coincidence, but it appears that the quantity $\frac{\sqrt{h}}{d}$ in these two last-mentioned cases is nearly the same, but in

* But in these latter the specific gravity is evidently too high in the case of acetone, and in a less degree with butyric ether.

others the divergence is found to be greater. This also requires further investigation.

It must, however, be remembered that in all these the limit is derived solely from A and H. It is evident, then, that if either of these indices for A or H are in error, or *are affected by anomalous dispersion*, all the rest will be affected. Yet, considering the nature of the investigation,—which is, given certain indices to find the rest—it is evident that the fewer which are assumed as data the more confidence we may have, if we find that the rest are all calculable within reasonable limits. This, then, is the result of the present investigation: given two indices, all the rest can be found within limits, which are in a considerable number of instances very fair approximations to the truth. As, however, in the cases observed the outstanding differences are in the same direction, and increase apparently towards the more refrangible end of the spectrum, we have an indication of law, which may be sought for both in the circumstances of the experiment and in the mathematics of the problem.

It will be observed that the effect of substitution on the quantity $\nu-1$ is very marked indeed. This is shown in the case of ethyl sulphide and ethyl thiocarbamide, and still more in that of the substitution of iodine and bromine for chlorine. Iodine is peculiarly effective in increasing the specific gravity in far greater proportion than it raises the value of the refractive and dispersive powers. No simple relation between either density and $\nu-1$ or the quantity denoted by h is as yet apparent. I have tried the square and cube, and the square root and cube root of h , as well as the simple power. I have noticed above that $\frac{\sqrt{h}}{d}$ is in case

of some isomeric bodies nearly a constant, but this may be a mere coincidence. It is, however, worth noticing, as $\sqrt{h}$ enters the coefficient k of Airy's equation cited above. When the logarithms are at hand, the calculations are so simple that even in the absence of any theoretical considerations it seemed worth while to try them.

It will be observed that the equation, by (ζ) and (η),

$$a \sin \theta = \sin m\theta$$

is impossible if $a \sin \theta$ is greater than unity. Now as a is the ratio of two wave-lengths in free æther, denoted in this investigation by $\lambda : \lambda_1$, we may ask what happens if the ratio of λ_1 the upper wave-length to λ the lower exceeds the ratio unity. Now in all cases yet examined, with the exception of selenium, this shorter wave-length is beyond violet and indeed the visible spectrum. In selenium it must lie somewhere near E; in solid phosphorus and sulphur it is beyond the furthest limit of the spectrum towards its more refrangible end, given by Prof. Langley, *i. e.* 0.3727. The results are given for these three substances in Table IV. annexed. It will be seen that phosphorus reaches the limit at about 2684 and sulphur at nearly 2664. We may observe as a coincidence that the behaviour of selenium in relation to light is remarkable, while its red colour shows that the violet end of the spectrum is absorbed. The results in Table V. are supplemental, calculated to the nearest minute, from determinations recently supplied by Dr. Gladstone, of ν for water and alcohol.

Abstract of Results.

1. That the relationship between the limit of refraction (ν) found by the equation $a \sin \theta = \sin m\theta$, where a is the ratio of two wave-lengths in free æther and m the corresponding ratio in the medium, give a value which has the property expressed by the equation $\frac{\nu-1}{d}$ a constant, where d is the density of the medium and ν its limit of refraction at the same temperature.

2. That in isomeric bodies the same relation obtains closely in a large number of the bodies examined.

3. In all the cases examined ν is a quantity not *very* far below μ_A .

4. That the substitution of one chemical element for another has a very great influence on the quantity $\frac{\nu-1}{d}$, and substances with high chemical equivalent have, as far as examined, a far greater influence in increasing the density than in raising the limit.

5. That the equation $a \sin \theta = \sin m\theta$ gives in the cases

examined an approximate value for all the other indices, two being assumed as data. In the case of rock-salt this holds good far down in the invisible heat-spectrum, and also in the ultra-violet, but fails somewhat at a certain point in the flint-glass spectrum, and also, to a less degree, at the upper end of the visible spectrum of bisulphide of carbon.

It is evident that for a certain value of a and θ the equation $a \sin \theta = \sin m\theta$ becomes impossible. This would mean that there is an upper limit which is given by a certain value of wave-length, beyond which the formula gives impossible results. In the case of selenium only, of the substances examined, is this limit within the visible spectrum. The analogy with the critical angle of total reflexion gives this circumstance considerable interest.

It is evident, then, in the present state of our data, that in all cases examined the formula of Sir Geo. Airy gives an approximate value of an index by means of two others, and in this way they can be calculated; but that, as a rule, the lower indices come out too high as compared with the upper. A cause for this may perhaps be suggested in the heating of the medium due to the absorption of the rays; and as there seems to be evidence of absorption of short waves above the longer ones, given by recent stellar photometric determinations, this absorption would perhaps, if included in the conditions of the problem, account for some of the outstanding difference. This and anomalous dispersion—itsself apparently depending on absorption—opens an interesting field of inquiry, and in this direction I propose to pursue the investigation.

Since the above was written I have been informed by Dr. Gladstone that he in some cases used a screen of solution of alum, but found that practically nothing was gained by its use. This fact, then, must be taken into account in any attempt to explain the outstanding differences between theory and observation.

TABLE I.—LANGLEY'S FLINT-GLASS PRISM.

Line.	Wave-length.	Index.	θ from sin.	θ from arc.	θ from sin.	θ from arc.
O.....	0.34400	1.6266	28° 21' 6"	28° 22' 50"	29° 16' 30"	29° 17' 10"
H ...	0.39679	1.6070	24 18 40	do.	25 5 0	
F.....	0.48606	1.5899	19 38 10	19 38 7	20 14 50	20 15 33
D.....	0.58890	1.5798	16 6 20	16 6 26		
O.....	0.65618	1.5757	14 24 57	14 24 57	14 51 15	14 52 25
A.....	0.76009	1.5714	12 24 20	12 24 20		
	0.815	1.5697	11 33 46	11 33 42		
	0.850	1.5687	11 4 50	11 4 43		
	0.890	1.5678	10 34 30	10 34 28		
	0.910	1.5674	10 20 30	10 20 23		
	0.940	1.5668	10 0 21	10 0 21		
	1.130	1.5636	8 18 43	8 18 23		
	1.270	1.5616	7 23 19	7 22 53		
	1.360	1.5604	6 53 56	6 53 15		
	1.540	1.5576	6 9 30	6 8 31	6 20 30	6 20 13
	1.580	1.5572	5 56 0	5 54 20		
	1.810	1.5544	5 10 40	5 9 10	5 19 50	5 19 7
	1.870	1.5535	5 0 40	4 59 10		
	1.980	1.5520	4 43 55	4 42 20		
	2.030	1.5515	4 37 11	4 35 17	4 44 32	4 41 1

TABLE II.—ROCK-SALT PRISM.

(Prof. Langley's Determinations, Phil. Mag.
May 1886, no. 132.)

Line.	Wave-length.	Index.	θ from sine.	θ from arc.	Difference.	Limit of Refract.	
						Sine.	Arc.
M ...	0.3727	1.57486	24 46 35	24 46 45	+0 10	1.52570	
L.....	0.3820	1.57207	24 8 5	24 8 19	0 14		
H ₂ ...	0.3933	1.56920	23 23 50	23 24 8	0 18		
H ₁ ...	0.3968	1.56833	23 10 49	datum.			
G ...	0.4303	1.56133	21 17 0	21 17 7	0 7		
F.....	0.4861	1.55323	18 44 47	18 44 47	0 0		
b ₄ ...	0.5167	1.54991	17 35 41	17 35 40	-0 1		
b ₁ ...	0.5183	1.54975	17 32 19	17 32 16	-0 3		
D ₁ ...	0.5889	1.54418	15 22 49	15 22 49	0		
D ₂ ...	0.5895	1.54414	15 21 50	15 21 52	+0 2		
C.....	0.6562	1.54051	13 46 12	13 46 12	0	1.5251	1.5249
B.....	0.6867	1.53919	12 8 49	12 8 50	+0 1		
A.....	0.7601	1.53670	11 51 12	11 51 13	+0 1		
ρ	0.94	1.5328	9 33 53	9 33 58	+0 5		
ϕ	1.13	1.5305	7 56 42	7 56 40	-0 2		
ψ	1.38	1.5287	6 29 49	6 29 51	+0 2		
Q.....	1.82	1.5268	4 55 24	4 55 14	-0 10		

H₁ is found from indices of H₁ and A, and from H all the other lines are deduced. Molecular distance $h=0.032570$; $\mu_H-3(\mu_F-\mu_B)=1.52621$.

TABLE III.

Bisulphide of Carbon.							
Temp. <i>t.</i>	Sp. Grav. <i>d.</i>	Index A. μ_A .	Index H. μ_H .	Angle A. θ_H .	Limit. ν .	Mol. dist. <i>h.</i>	Specific Limit. $\frac{\nu-1}{d}$.
15°	1.2909	1.6227	1.7159	18.38 2	1.5944	.048505	46048
23.0	1.2594	1.6070	1.6972	18 25 50	1.5799	.04844	46046
38.0	1.2494	1.6026	1.6922	18 25 30	1.5752	.048559	46038
Another Specimen.							
10.0	1.2793	1.6153	1.7078	18 37 43	1.5869	.048673	45885
24.5	1.2593	1.6045	1.6954	18 30 45	1.5770	.048616	45819
Comparison of Values of Limit calculated from sine θ_H and arc θ_H with corresponding angles for CS ₂ at 10°.— $\theta_H=37^\circ 44' 40''$.							
	Line A.	B.	C.	D.	E.	F.	G.
Sine ...	18 37 43	20 42 50		24 19 59		29 54 4	34 19 40
Limit...	1.5870			1.5862		1.5843	1.5847
Arc ...	18 39 46	20 41 52		24 18 52		29 55 58	34 16 52
Limit...	1.5869			1.5861		1.5849	1.5848
Another value obtained by interpolation, $\theta_H=37^\circ 29' 20''$.							
Sine ...	18 35 20	20 40 10	21 40 40	24 16 50	27 23 30	29 54 50	34 13 40
Arc ...	18 35 10	20 40 40	21 40 0	24 15 30	27 21 10	29 51 50	34 11 10
The value of ν lies between 1.5867 and 1.5852.							
Mint Hydrocarbon.							
Temp. <i>t.</i>	Sp. Grav. <i>d.</i>	Index A. μ_A .	Index H. μ_H .	Angle A. θ_A .	Limit. ν .	Mol. dist. <i>h.</i>	Specific Limit. $\frac{\nu-1}{d}$.
6.5	0.8926	1.4728	1.4988	11 4 50	1.4632		51893
25.0	0.8820	1.4650	1.4901	10 58 0	1.4561		51712
Benzene.							
2.0	0.8979	1.5021	1.5460	13 56 40	1.4873	.039219	54272
23.7	0.8760	1.4893	1.5320		1.4725	.039122	54328
28.6	0.8709	1.4860	1.5279	13 50 35	1.4720	.038892	54196

Table III. (*continued*).

Benzene.—Another Specimen.							
Temp. <i>t.</i>	Sp. Grav. <i>d</i>	Index A. μ_A	Index H. μ_H	Angle A. θ_A	Limit. <i>v.</i>	Mol. dist. <i>h.</i>	Specific Limit. $\frac{v-1}{d}$
10.0	0.8868	1.4935	1.5355	13 43 10	1.4792	.038802	54037
21.5	0.8773	1.4887	1.5304	13 41 45	1.4745	.038850	54077
Styrolene.							
11.0	0.9409	1.5208	1.5693	14 1 0	1.5057	.038848	53747
Another Specimen.							53853
Cresol.							
23.0	1.039	1.5316	1.5787	14 45 0	1.5137	.040776	49442
Metacresol.							
19.0	1.033	1.5257	1.5726	14 13 50	1.5102	.039395	49390
Benzil Alcohol.							
22.0	1.0412	1.5278	1.5710	13 58 0	1.5150	.038089	49467
Methyl Citraconate.							
15.5	1.1164	1.4442	1.4721	11 32 0	1.4345		38920
Methyl Meseaconate.							
16.0	1.1246	1.4492	1.4813	12 19 0	1.4380		38938
Picoline.							
23.5	0.94093	1.4912	1.5317	13 29 0	1.4774	.038247	50726
Aniline.							
13.0	1.016	1.5695	1.6336	16 9 0	1.5488	.043342	54016
Another specimen.							
7.5	1.0322	1.5780	1.6449	16 25 0	1.5565	.043940	53920
Benzil Chloride.							
7.0	1.099	1.5314	1.5764	13 59 0	1.5160	0.37148	46592
Chlorotoluine.							
19.0	1.0761	1.5173	1.5613	13 54 0	1.5027	.038701	46717

Table III. (*continued*).

Acetone.							
Temp. <i>t.</i>	Sp. Grav. <i>d.</i>	Index A. μ_A	Index H. μ_H	Angle A. θ_A	Limit. ν	Mol. dist. <i>h.</i>	Specific Limit. $\frac{\nu-1}{d}$
*25.5	0.8117 at 15°	1.3540	1.3706	9 25 0	1.3479	.024733	42860
Butyric Ether.							
*23.0	0.8778 at 20°	1.3850	1.4669	9 24 0	1.3778	.027995	43039
Allyl Alcohol.							
23.0	0.8563	1.4054	1.4289	10 44 55	1.3695	.025438	46304
Allyl Sulphide.							
11.0	0.8544	1.4531	1.4811	11 30 40	1.4434		51837
Ethyl Thiocarbamide.							
18.0	1.0030	1.5040	1.5477	13 13 0	1.4890		48794
Orthobromotoluine.							
.....	1.4192	1.5502	1.5981	14 3 50	1.5299		37340
Compare this with benzil chloride above					1.5160		46592
Isobutyl Chloride.							
19.0	0.8626	1.3939	1.4111	8 57 30	1.3882		45004
Isobutyl Iodide.							
.....	1.5982	1.4874	1.5240	12 53 0	1.4749		29717
Mercuric Methyl.							
30.0	2.966	1.5229	1.5683	14 5 0	1.5076		17365
Bromopiecin.							
13.0	2.816	1.5736	μ_D 1.5831	14 0 0	1.5246		18612

* It will be seen that in both these *d* is too great.

TABLE IV.

Substance.	Lower Index.	Upper Index.	Angle θ_A .	Limit.	Limiting Wave-length.
Selenium {	μ_A . 2.653	μ_D . 2.980	θ_A . 44° 9' 0"	ν . 2.1353	5295.7
Solid Sulphur {	μ_A . 1.9024	μ_E . 1.9527	20° 30' 0"	1.8621	2663.8
Solid Phosphorus {	μ_A . 2.1059	μ_E . 2.1442	20° 40' 0"	2.0611	2683.8

TABLE V.

Sp. g.	μ_A .	μ_H .	ν .	$\frac{\nu-1}{d}$.
Water. 1.000	1.32924	1.34393	1.3249	3249
Alcohol. 0.7919	1.3585	1.3735	1.3531	44589

XXV. *The Temperature at which Nickel begins to lose suddenly its Magnetic Properties.* By HERBERT TOMLINSON, B.A.*

It has long been known that nickel, like iron, begins at a certain temperature to rapidly lose its magnetic properties, and that the critical temperature for the former metal is much lower than for the latter. According to Faraday, nickel loses its magnetic permeability about 330° to 340° C.; according to Becquerel, about 400° C.; according to Pouillet, about 350° C.; and according to Chrystal, about 400° C. Berson, however, seems to have been the first† to publish a curve showing the relation between magnetic induction and temperature right up to the point at which the former ceases practically to exist. The author has also, independently of Berson, drawn up curves of a similar kind which have not as yet been published, and which he ventures to offer to the Physical Society, because they not only supplement Berson's results, but they seem also to partly explain why different observers have obtained such widely differing temperatures for the point of *nil* permeability‡.

In the axis of a magnetizing solenoid, and perpendicular to the magnetic meridian, was placed a nickel wire, 30 centim. in length and 0.0053 square centim. in section. The solenoid consisted of cotton-covered copper wire of $\frac{1}{20}$ inch in diameter,

* Read February 25, 1888.

† *Ann. de Phys. et de Chim.* vol. vii. (1886).

‡ That is *practically* nil. The experiments of Faraday seem to show that the permeability never *entirely* vanishes.