ART. XXXIII.—*On the Indices of Refraction of certain Compound Ethers*; by JOHN H. LONG.

ABOUT two years ago, while at work in the laboratory of the University of Tübingen, I undertook the determination of the Indices of Refraction of a number of Ethers of the $C_nH_{2n}O_2$ series. This work was commenced at the suggestion of Professor Lothar Meyer, who was at the same time engaged in an investigation concerning the rates of transpiration of these and other bodies. It might also be remarked that the same substances were being used by Herrn Emil Elsässer for the determination of specific gravity and coefficient of expansion, and his results I have made use of in the calculation of the tables found below.

Other duties prevented the publication of my results at the time, but the elegant work of Brühl,* which has since appeared, having added a new interest to the subject of refraction, I deem it not too late to make them known now. The method employed was essentially that of Landolt.† A large Meyerstein spectrometer, kindly loaned me by Professor v. Reusch of the Tübingen physical laboratory, permitted results exact to four decimal places of n (as explained below) to be readily obtained. The fifth decimal place is in most cases uncertain.

As source of light I used the sodium flame and the refractive indices for the D line were determined for several different temperatures. This was accomplished as follows: The hollow glass prism containing the liquid to be examined, together with its metallic support, was placed on a hot iron plate and left there until the temperature of the liquid had risen (in most cases) to about $30^\circ C.$, as shown by the small thermometer firmly secured by a cork in the orifice of the prism. Then the prism and support were replaced on the spectrometer, allowed to remain a few minutes, when the final adjustments were made and the observations commenced. The readings were made from degree to degree, and continued until the temperature of the liquid in the prism had fallen to that of the room. The thermometer used had been previously carefully compared with a normal thermometer in the possession of Professor Meyer and a table of corrections thus obtained, so that the temperatures given may be looked upon as exact to 0.1° .

The indices were determined by the method of minimum deviation, according to the formula

* J. W. Brühl: Die chemische Constitution organischer Körper in Beziehung zu deren Dichte u. Vermögen d. Licht fortzupflanzen. *Liebig's Annalen*, cc, 139; cciii, 1, 255 and 363. See also this *Journal*, Jan., 1881. page 70.

† *Pogg. Ann.*, Bd. cxvii, 353.

$$n = \frac{\sin \frac{A+d}{2}}{\sin \frac{A}{2}}$$

where d is the observed angle of minimum deviation and A the refractive angle of the prism. This latter was determined before each observation (as the sides of the prism were formed of glass plates fastened by rubber bands) and varied between $60^{\circ} 2' 30''$ and $60^{\circ} 3' 30''$.

In every case at least two complete sets of observations were made for each substance and the mean of the results, which never showed variations beyond the fifth decimal place, was taken. The following table contains these results.

Under T I have given the temperature in degrees Cent. at which the observations were made. Under n are given the indices, and under *diff.* the variations in the same for a change in temperature of one degree. In every case the boiling point of the ether in question is given, and when the same was determined under diminished pressure, this latter element is given. In other cases the usual barometric height in Tübingen—about 735^{mm}—is to be understood.

METHYL FORMATE.		
Bp = 32°·8		
T.	n.	diff.
20	1·34386	
19	1·34430	·00044
18	1·34473	43
17	1·34516	43
16	1·34559	43
15	1·34601	42

PROPYL ACETATE.		
Bp = 87°·8–88°·2 P, 470 ^{mm}		
T.	n.	diff.
22	1·38352	
21	1·38404	·00052
20	1·38456	52
19	1·38507	51
18	1·38558	51
17	1·38608	50

PROPYL FORMATE.		
Bp = 67°–67°·3 P, 431 ^{mm}		
T.	n.	diff.
23	1·37604	
22	1·37656	·00052
21	1·37706	50
20	1·37756	50
19	1·37806	50
18	1·37855	49
17	1·37904	49

METHYL PROPIONATE.		
Bp = 79°·5–80°		
T.	n.	diff.
20	1·37763	
19	1·37822	·00059
18	1·37875	53
17	1·37927	52
16	1·37980	53
15	1·38032	52

ISOBUTYL FORMATE.		
Bp = 99°–99°·4		
T.	n.	diff.
22	1·38641	
21	1·38693	·00052
20	1·38745	52
19	1·38796	51
18	1·38845	49
17	1·38893	48
16	1·38941	48

ETHYL PROPIONATE.		
Bp = 81°·4–82° P, 402 ^{mm}		
T.	n.	diff.
20	1·38421	
19	1·38471	·00050
18	1·38520	49
17	1·38568	48
16	1·38616	48
15	1·38663	47

PROPYL PROPIONATE.			
Bp = 101°·5–102°		P, 384 ^{mm}	
T.	n.		diff.
23	1·39199		
22	1·39253	·00054	
21	1·39305	52	
20	1·39356	51	
19	1·39405	49	
18	1·39452	47	
17	1·39497	45	

ETHYL ISOBUTYRATE.			
Bp = 107°–107°·3			
T.	n.		diff.
25	1·38537		
24	1·38589	·00052	
23	1·38641	52	
22	1·38693	52	
21	1·38745	52	
20	1·38797	52	

ISOBUTYL PROPIONATE.			
Bp = 135°·2–135°·5			
T.	n.		diff.
20	1·39748		
19	1·39793	·00045	
18	1·39838	45	
17	1·39882	44	
16	1·39925	43	

PROPYL ISOBUTYRATE.			
Bp = 130°·5–131°			
T.	n.		diff.
25	1·39369		
24	1·39414	·00045	
23	1·39459	45	
22	1·39504	45	
21	1·39549	45	
20	1·39593	44	
19	1·39637	44	

AMYL PROPIONATE.			
Bp = 159°·5–160°			
T.	n.		diff.
23	1·40523		
22	1·40567	·00044	
21	1·40610	43	
20	1·40653	43	
19	1·40696	43	
18	1·40738	42	
17	1·40780	42	

ISOBUTYL ISOBUTYRATE.			
Bp = 144°–145°			
T.	n.		diff.
25	1·39775		
24	1·39819	·00044	
23	1·39863	44	
22	1·39906	43	
21	1·39949	43	
20	1·39992	43	
19	1·40034	42	

ISOBUTYL BUTYRATE.			
Bp = 154°·5–155°			
T.	n.		diff.
20	1·40443		
19	1·40485	·00042	
18	1·40527	42	
17	1·40570	43	
16	1·40612	42	
15	1·40654	42	

AMYL ISOBUTYRATE.			
Bp = 166°–166°·5			
T.	n.		diff.
25	1·40548		
24	1·40591	·00043	
23	1·40634	43	
22	1·40676	42	
21	1·40718	42	
20	1·40759	41	
19	1·40800	41	
18	1·40841	41	

AMYL BUTYRATE.			
Bp = 178°–178°·5			
T.	n.		diff.
22	1·41010		
21	1·41052	·00042	
20	1·41094	42	
19	1·41135	41	
18	1·41176	41	
17	1·41217	41	

PROPYL VALERATE.			
Bp = 155°·5–156°			
T.	n.		diff.
24	1·40182		
23	1·40229	·00047	
22	1·40275	46	
21	1·40321	46	
20	1·40366	45	
19	1·40411	45	
18	1·40455	44	

METHYL ISOBUTYRATE.			
Bp = 89°·8–90°			
T.	n.		diff.
26	1·38082		
25	1·38136	·00054	
24	1·38190	54	
23	1·38243	53	
22	1·38296	53	
21	1·38348	52	
20	1·38399	51	

ISOBUTYL VALERATE.			
Bp = 169°–169°·4			
T.	n.		diff.
25	1·40393		
24	1·40441	·00048	
23	1·40489	48	
22	1·40536	47	
21	1·40583	47	
20	1·40630	47	

From the above table it is seen, as has already been shown by Landolt and others, that the increase in n for one degree C. is in the mean about .00045. As a rule this difference is not constant, but increases with the temperature; in a few cases, however, as for instance ethyl isobutyrate and isobutyl butyrate there are no second differences. Although the differences vary from .00041 to .00059, they seem quite irregular, and it is not easy to connect them with any chemical property of the bodies in question, and still more difficult is it to account for the appearance of the second differences in some cases and in others not. But I shall not attempt a further explanation of these points here.

Of the above-named ethers the refractive indices of propyl acetate alone have been determined, as far as I am aware. Brühl gives for this for a sample boiling between 99° – 101° the index $n_D = 1.38438$ at 20° , and for another portion boiling from 97° – 99° $n_D = 1.38360$. It will be noticed that the first of these values corresponds very closely with that obtained by me. Indeed the agreement is better than one might expect, when the great liability of the ether to dissociation is taken into consideration. Brühl mentions this fact, and I have reason to believe that the sample used by me had likewise been slightly decomposed by the fractional distillation.

In order to show the results obtained above, in their most general aspect, as well as for the purpose of better comparison with the work of others, I have arranged them in a more complete form below. In the columns headed d are contained the densities of the substances for each degree of temperature, calculated as explained at the outset. Under n are given the refractive indices to four places, the somewhat uncertain fifth place being omitted. Under $\frac{n-1}{d}$ is given the "specific refractive energy," and under $M \left(\frac{n-1}{d} \right)$ the "molecular refractive energy" for each compound at the various temperatures. M represents the molecular weight of the ether in question. I use these terms in the sense in which they have been employed by Dale & Gladstone and Landolt, and they need no further explanation. Propyl acetate I here omit, as I do not know the variations in its density with the temperature.

The quotients $\frac{n-1}{d}$ are on the whole quite satisfactory, although the fourth decimal places are not always the same. Some seem constant with the temperature, two increase, while the others are seen to decrease. The same irregularity has been already noticed by Landolt and Wüllner,* yet it still remains to be explained. In the above ethers it will be noticed

<i>T</i>	<i>d</i>	<i>n</i>	$\frac{n-1}{d}$	$M\left(\frac{n-1}{d}\right)$	<i>T</i>	<i>d</i>	<i>n</i>	$\frac{n-1}{d}$	$M\left(\frac{n-1}{d}\right)$
METHYL FORMATE.					ISOBUTYL PROPIONATE.				
M = 60 <i>d</i> ₀ = ·99840					M = 130 <i>d</i> ₀ = ·88759				
15	·9767	1·3460	·3543	21·26	16	·8732	1·3992	·4572	59·43
16	·9753	1·3456	·3544	21·26	17	·8722	1·3988	·4572	59·43
17	·9738	1·3452	·3545	21·27	18	·8713	1·3984	·4572	59·43
18	·9723	1·3448	·3546	21·28	19	·8704	1·3979	·4571	59·42
19	·9708	1·3443	·3547	21·28	20	·8694	1·3975	·4572	59·43
20	·9694	1·3438	·3547	21·28					
PROPYL FORMATE.					AMYL PROPIONATE.				
M = 88 <i>d</i> ₀ = ·91838					M = 144 <i>d</i> ₀ = ·88767				
17	·8996	1·3790	·4213	37·07	17	·8729	1·4078	·4672	67·27
18	·8985	1·3785	·4213	37·07	18	·8721	1·4074	·4671	67·27
19	·8974	1·3780	·4212	37·07	19	·8712	1·4070	·4671	67·27
20	·8962	1·3775	·4212	37·07	20	·8703	1·4065	·4671	67·27
21	·8951	1·3770	·4212	37·07	21	·8694	1·4061	·4671	67·27
22	·8940	1·3765	·4211	37·06	22	·8685	1·4057	·4671	67·27
23	·8928	1·3760	·4212	37·07	23	·8676	1·4052	·4671	67·27
ISOBUTYL FORMATE.					ISOBUTYL BUTYRATE.				
M = 102 <i>d</i> ₀ = ·88543					M = 144 <i>d</i> ₀ = ·88178				
16	·8697	1·3894	·4477	45·67	15	·8674	1·4065	·4686	67·49
17	·8687	1·3889	·4477	45·67	16	·8665	1·4061	·4687	67·49
18	·8677	1·3884	·4476	45·66	17	·8655	1·4057	·4688	67·50
19	·8667	1·3879	·4476	45·66	18	·8645	1·4053	·4688	67·50
20	·8657	1·3874	·4475	45·64	19	·8636	1·4049	·4689	67·52
21	·8647	1·3869	·4474	45·64	20	·8627	1·4045	·4689	67·52
22	·8637	1·3864	·4474	45·64					
METHYL PROPIONATE.					AMYL BUTYRATE.				
M = 88 <i>d</i> ₀ = ·93725					M = 158 <i>d</i> ₀ = ·88231				
15	·9277	1·3803	·4099	36·07	17	·8673	1·4122	·4753	75·10
16	·9271	1·3798	·4097	36·05	18	·8664	1·4118	·4753	75·10
17	·9265	1·3793	·4094	36·03	19	·8655	1·4114	·4753	75·10
18	·9259	1·3788	·4091	36·00	20	·8646	1·4110	·4754	75·11
19	·9252	1·3782	·4088	35·97	21	·8637	1·4105	·4753	75·10
20	·9246	1·3776	·4084	35·94	22	·8628	1·4101	·4753	75·10
ETHYL PROPIONATE.					METHYL ISOBUTYRATE.				
M = 102 <i>d</i> ₀ = ·91238					M = 102 <i>d</i> ₀ = ·91118				
15	·8959	1·3866	·4315	44·01	20	·8893	1·3840	·4318	44·04
16	·8948	1·3862	·4316	44·02	21	·8882	1·3835	·4318	44·04
17	·8937	1·3857	·4316	44·02	22	·8871	1·3830	·4317	44·03
18	·8926	1·3852	·4316	44·02	23	·8860	1·3824	·4316	44·02
19	·8915	1·3847	·4315	44·01	24	·8849	1·3819	·4316	44·02
20	·8904	1·3842	·4315	44·01	25	·8838	1·3814	·4315	44·01
					26	·8827	1·3808	·4314	44·00
PROPYL PROPIONATE.					ETHYL ISOBUTYRATE.				
M = 116 <i>d</i> ₀ = ·90191					M = 116 <i>d</i> ₀ = ·89037				
17	·8857	1·3950	·4460	51·73	20	·8697	1·3880	·4461	51·75
18	·8848	1·3945	·4459	51·72	21	·8686	1·3875	·4461	51·75
19	·8838	1·3940	·4458	51·72	22	·8676	1·3869	·4460	51·73
20	·8828	1·3935	·4457	51·71	23	·8665	1·3864	·4459	51·73
21	·8818	1·3930	·4457	51·70	24	·8655	1·3859	·4459	51·72
22	·8809	1·3925	·4456	51·69	25	·8644	1·3854	·4459	51·72
23	·8799	1·3920	·4455	51·68					

<i>T</i>	<i>d</i>	<i>n</i>	$\frac{n-1}{d}$	$M\left(\frac{n-1}{d}\right)$	<i>T</i>	<i>d</i>	<i>n</i>	$\frac{n-1}{d}$	$M\left(\frac{n-1}{d}\right)$
PROPYL ISOBUTYRATE. M = 130 <i>d</i> ₀ = '89299					PROPYL VALERATE. M = 144 <i>d</i> ₀ = '88092				
19	'8748	1'3964	'4531	58'90	18	'8652	1'4046	'4676	67'34
20	'8738	1'3959	'4531	58'90	19	'8643	1'4041	'4676	67'33
21	'8728	1'3955	'4531	58'90	20	'8634	1'4036	'4675	67'32
22	'8719	1'3950	'4530	58'89	21	'8626	1'4032	'4674	67'31
23	'8709	1'3946	'4531	58'90	22	'8617	1'4028	'4674	67'31
24	'8699	1'3941	'4530	58'89	23	'8608	1'4023	'4674	67'30
25	'8690	1'3937	'4531	58'90	24	'8599	1'4018	'4673	67'29
ISOBUTYL ISOBUTYRATE. M = 144 <i>d</i> ₀ = '87496					AMYL ISOBUTYRATE. M = 158 <i>d</i> ₀ = '87597				
19	'8584	1'4003	'4663	67'15	18	'8598	1'4084	'4750	75'05
20	'8575	1'3999	'4664	67'16	19	'8589	1'4080	'4750	75'05
21	'8566	1'3995	'4664	67'16	20	'8580	1'4076	'4751	75'06
22	'8557	1'3991	'4664	67'16	21	'8571	1'4072	'4751	75'07
23	'8548	1'3986	'4663	67'15	22	'8562	1'4068	'4751	75'07
24	'8539	1'3982	'4663	67'15	23	'8553	1'4063	'4750	75'06
25	'8530	1'3978	'4663	67'15	24	'8544	1'4059	'4751	75'06
ISOBUTYL VALERATE. M = 158 <i>d</i> ₀ = '87360					25	'8535	1'4055	'4751	75'07
20	'8558	1'4063	'4748	75'01					
21	'8549	1'4058	'4747	75'01					
22	'8540	1'4054	'4747	75'00					
23	'8531	1'4049	'4746	74'99					
24	'8522	1'4044	'4745	74'98					
25	'8513	1'4039	'4745	74'98					

that the constancy of $\frac{n-1}{d}$ is attained in eight cases, while in an equally great number it is not. An attempt to connect this peculiarity with others of the same bodies has not been successful.

An opportunity is afforded by the above experiments of comparing the physical characteristics of some of the butyrates and isobutyrate. The constants for methyl and ethyl butyrate are taken from Landolt's paper,[†] *n*_D being computed by means of the formula of Cauchy,

$$n_D = A + \frac{B}{\lambda_D^2}$$

in which A is the coefficient of refraction, and B that of dispersion. For the wave-length of the line D, I have used the mean value given by Wüllner,[‡] expressed in ten-thousandths of a millimeter, $\lambda_D = 5.893$.

From Landolt I take

Methyl butyrate	A = 1'37879	B = 0'35077
Ethyl butyrate	A = 1'38580	B = 0'35310

* Lehrbuch d. Experimentalphysik, vol. ii, p. 150.

† Pogg., cxvii. 545, where the values for A and B are given.

‡ Lehrbuch, etc., vol. ii, p. 136.

Making the necessary calculations I find the values as in the following table:

	Bp	d_{20}	n_{20}
{ Methyl butyrate	103–104°	·8976	1·3889
{ Methyl isobutyrate	90°	·8893	1·3840
{ Ethyl butyrate	114°	·8906	1·3960
{ Ethyl isobutyrate	107°	·8697	1·3880
{ Isobutyl butyrate	155°	·8627	1·4045
{ Isobutyl isobutyrate	144–145°	·8575	1·3999
{ Amyl butyrate	178°	·8646	1·4110
{ Amyl isobutyrate	166°	·8580	1·4076

As might be expected, the constants in the case of the iso compounds are in every instance lower than in those of the corresponding normals. Here as in several compounds examined by Brühl, the characteristic differences of ethers of normal and iso acids are seen to extend to their action on light.

It will not be without interest to find what values for the atomic refractive power can be deduced from the above observations. For this purpose I have grouped the ethers as in the following table. Arranging the isomers together, there are seven groups with different molecular weights, and for the molecular refraction of each I have placed the mean value of those of the several members of each group.

		$M \left(\frac{n-1}{d} \right)$	diff. for CH ₂
Methyl formate.....	C ₂ H ₄ O ₂	21·28	
Propyl formate	C ₄ H ₈ O ₂	36·57	7·65
Methyl propionate ..			
Ethyl propionate ..	C ₆ H ₁₀ O ₂	44·56	7·99
Isobutyl formate....			
Methyl isobutyrate..	C ₆ H ₁₂ O ₂	51·72	7·16
Propyl propionate..			
Ethyl isobutyrate..	C ₇ H ₁₄ O ₂	59·16	7·44
Isobutyl propionate			
Propyl isobutyrate..	C ₈ H ₁₆ O ₂	67·32	8·16
Amyl propionate ..			
Isobutyl butyrate..	C ₉ H ₁₈ O ₂	75·06	7·74
Isobutyl isobutyrate			
Propyl valerate.....			
Amyl butyrate			
Amyl isobutyrate ..			
Isobutyl valerate ..			
Mean diff. for CH ₂ = 7·69.			

It thus appears that the differences for CH₂ from group to group are not quite constant, but the variations are not greater than one might expect when the character of the compounds is taken into consideration. The average of the differences gives for the refractive power of CH₂ 7·69. Substituting this in the different groups, we find for O₂ the refractive powers 5·90, 5·81, 6·11, 5·58, 5·33, 5·80 and 5·85. Of course it is not intended that these numbers represent the atomic refraction in

any particular groups. They are simply mean values obtained by combining the numbers $M \left(\frac{n-1}{d} \right)$ of the last table in a certain way. From other combinations it is plain that slightly different values would be obtained. The average of the results just given makes 5.77 the refractive power of O_2 , that is of one linking and one saturating O as shown by Brühl. It will be seen that these values do not differ greatly from the mean refractive equivalents as given by Landolt—i. e., 7.60 for CH_2 and 3.00 for O, which it must be remembered were calculated from numbers differing as widely perhaps as the above. Whether these variations depend for their explanation on the possible impurity of the liquids examined, or whether they are to a greater extent due to peculiarities of each individual compound, is as yet not quite plain. It seems probable, however, in view of all that has been thus far done on the subject, that the latter is the more plausible supposition. But it is only by refined and extended investigations of various physical properties and correlation of the results thus obtained, that the complete solution of the problem may be expected. For this purpose, I had wished to make use of some of the results obtained by Pribram and Handl on the transpiration of liquids (Wien. Sitzungsbr. 80), but unfortunately I was unable to obtain this journal.

There are many other interesting peculiarities of these ethers which might be mentioned, but their discussion belongs more properly to an investigation soon to be expected (or perhaps recently published), from Herrn Emil Elsässer, to whom, as was mentioned, I am indebted for the data from which I calculated the densities of the liquids corresponding to the different temperatures. To Professor Meyer I would also express my sincere thanks for assistance, without which the completion of the above experiments would not have been possible.

Wesleyan University, February, 1881.