

III. *On the Relations Between the Viscosity (Internal Friction) of Liquids and their Chemical Nature.*—Part II.

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With an Appendix on the Preparation of Ethers.

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IN the Bakerian Lecture for 1894 ('Phil. Trans.,' vol. 185 A, p. 397), we gave an account of our work on the viscosity of some seventy liquids at different temperatures between 0° and the ordinary boiling-point, and we discussed the interdependence of viscosity and chemical composition. Among the liquids dealt with on that occasion, there was no member of the important series of esters or ethereal salts, and, further, only one ether—ordinary ether or ethyl oxide—was included in the list.

We therefore thought it desirable, in order to make the investigation more complete, to obtain data for members of these two classes of organic substances. The physico-chemical relationships previously established made such determinations of particular interest. Among the various connections traced between chemical constitution and viscosity, one of the most striking was the different effect which oxygen exerted upon viscosity according to the different modes in which it was assumed to be associated with other atoms in the molecule. The influence which could be ascribed to hydroxyl-oxygen differs to a most marked extent from that of carbonyl-oxygen, and, although only three cases were studied, it appeared that ether oxygen, or oxygen linked to two carbon atoms, had also a value which differed considerably from those of oxygen in other conditions. There was thus an additional reason for making observations on esters and ethers, since both contain ether-oxygen.

In what follows we give the experimental values for the ten lowest fatty esters, carefully purified samples of which had been kindly placed at our disposal by Professor SYDNEY YOUNG, F.R.S., to whom we desire to tender our thanks.

At our suggestion Mr. R. E. BARNETT, B.Sc., Assoc. R.C.S., prepared five fatty ethers, and determined their viscosity. An Appendix to this paper is devoted to an account by him of the best methods of obtaining these liquids.

As we had the opportunity of making determinations of the viscosity of three different samples of isopentane and a sample of ethyl-benzene, which had been specially prepared and purified, the values obtained are also included in this paper.

The last section of the paper deals with the discussion of the values given by the esters and ethers according to the methods adopted in our previous communication.

8.3.97

ESTERS.

Before introduction into the glischrometer each sample was distilled from a small quantity of phosphoric oxide. In every case the boiling-point was almost constant during the distillation, and agreed closely with the value found by YOUNG and THOMAS ('Chem. Soc. Trans.', vol. 63, p. 1191, 1893). For this reason it was thought unnecessary to make determinations of any other physical constants for the purpose of gauging the purity of the samples, as the densities of liquid and vapour, the critical constants, &c., have been carefully determined by YOUNG and THOMAS, and may be obtained from the paper to which reference has been made. In each case we give the boiling-point as found by us, and as given by YOUNG and THOMAS (Y. and T.). In reducing the observations on viscosity we have employed the values of the density found by YOUNG and THOMAS, and the expressions for the thermal expansion given by ELSÄSSER ('LIEBIG'S Annalen,' 218, 316).

Methyl Formate. H.COOCH_3 .

Boiling-point constant at $31^\circ 87$. Bar., 762.6 millims. Corrected and reduced b.p. = $31^\circ 78$ ($31^\circ 8$, Y. and T.).

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0.57	100.17	.000066	.004269	0.59	100.09	.000066	.004258
6.38	100.11	.000060	.004006	6.40	100.05	.000069	.003992
10.90	100.10	.000072	.003815	10.86	100.03	.000072	.003804
15.63	100.03	.000075	.003635	15.64	99.96	.000075	.003617
20.15	99.97	.000078	.003476	20.15	99.90	.000078	.003458
25.52	99.94	.000081	.003310	25.52	99.85	.000081	.003286
29.25	99.90	.000083	.003203	29.26	99.81	.000083	.003177

In reducing the observations we have used the value $d(0^\circ/4^\circ) = 1.00319$ for the density, and the expression

$$V = 1 + .0_2135824 t + .0_410538 t^2 - .0_618085 t^3$$

for the thermal expansion.

Taking

$$\begin{array}{lll} \eta_1 = .004263 & \eta_3 = .003190 & \eta_2 \text{ (calculated)} = .003688, \\ t_1 = 0^\circ.58 & t_3 = 29^\circ.25 & t_2 \text{ (from curve)} = 13^\circ.67, \end{array}$$

we obtain the formula

$$\eta = \frac{0.144673}{(68.234 + t)^{.8325}},$$

which gives results in good agreement with the observed values.*

Ethyl Formate. $\text{H.COOCH}_2\text{CH}_3$.

Boiling-point constant at $54^\circ.66$. Bar., 771.1 millims. Corrected and reduced b.p. = $54^\circ.25$ (54.3 , Y. and T.).

Observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
$0^\circ.45$	100.19	.000053	.005028	$0^\circ.47$	99.74	.000053	.005020
$6^\circ.56$	100.81	.000057	.004662	$6^\circ.58$	100.77	.000057	.004650
$11^\circ.52$	100.70	.000060	.004415	$11^\circ.52$	100.64	.000060	.004403
$16^\circ.58$	100.61	.000063	.004177	$16^\circ.58$	100.51	.000063	.004166
$22^\circ.59$	100.59	.000066	.003916	$22^\circ.59$	100.50	.000066	.003904
$27^\circ.90$	100.96	.000069	.003708	$27^\circ.90$	100.90	.000069	.003689
$33^\circ.25$	100.92	.000073	.003507	$33^\circ.25$	100.84	.000073	.003495
$38^\circ.10$	100.89	.000075	.003351	$38^\circ.08$	100.79	.000075	.003337
$43^\circ.37$	100.78	.000078	.003187	$43^\circ.36$	100.72	.000078	.003169
$48^\circ.64$	100.63	.000081	.003038	$48^\circ.59$	100.54	.000082	.003023
$52^\circ.03$	100.54	.000083	.002956	$52^\circ.03$	100.47	.000083	.002928

The value $d(0^\circ/4^\circ) = 0.9480$ for the density, and the expression

$$V = 1 + .02130917 t + .0519198 t^2 + .0730497 t^3$$

for the thermal expansion, have been used in the reduction of the observations.

Taking

$$\begin{aligned} \eta_1 &= .005025 & \eta_3 &= .002942 & \eta_2 \text{ (calculated)} &= .003845, \\ t_1 &= 0^\circ.46 & t_3 &= 50^\circ.03 & t_2 \text{ (from curve)} &= 24^\circ.22, \end{aligned}$$

* To save space, it has been deemed unnecessary to give the comparisons between the observed and calculated values, as was done in the first paper. There is no longer any need to offer proof of the validity of the SLOTTE formula as an empirical expression of the relation between viscosity and temperature, especially in the case of liquids of the type now studied. It may be stated, however, that the comparison has been made in all cases, and that the general agreement is of the same order as that previously found.

we obtain the formula

$$\eta_t = \frac{22.2406}{(139.932 + t)^{1.7006}},$$

which gives results in good agreement with those observed.

Propyl Formate. $\text{H.COOCH}_2\text{CH}_2\text{CH}_3$.

Boiling-point constant at $80^\circ.77$. Bar., 757.0 millims. Corrected and reduced b.p. = $80^\circ.89$ ($80^\circ.9$, Y. and T.).

The following are the observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0.35	101.51	.000040	.006646	0.35	101.41	.000040	.006649
7.31	101.52	.000044	.006043	7.36	101.45	.000044	.006039
15.54	101.68	.000048	.005456	15.54	101.60	.000048	.005459
23.17	101.65	.000052	.004971	23.15	101.57	.000052	.004979
30.78	101.61	.000056	.004553	30.76	101.53	.000056	.004562
38.54	101.58	.000060	.004182	38.53	101.48	.000060	.004187
45.72	101.45	.000064	.003871	45.74	101.37	.000064	.003880
54.15	101.21	.000069	.003560	54.14	101.13	.000069	.003568
61.55	101.22	.000073	.003311	61.58	101.12	.000073	.003319
67.13	101.45	.000077	.003124	67.13	101.38	.000077	.003149
74.97	101.44	.000081	.002925	75.00	101.35	.000081	.002931
77.54	101.39	.000082	.002859	77.56	101.30	.000082	.002863

In reducing the observations we have used for the density at 0° the value 0.9287, and the expression

$$V = 1 + .0211903 t + .05201033 t^2 + .0715776 t^3$$

for the thermal expansion.

Taking

$$\begin{aligned} \eta_1 &= .006647 & \eta_3 &= .002861 & \eta_2 \text{ (calculated)} &= .004361, \\ t_1 &= 0^\circ.35 & t_3 &= 77^\circ.55 & t_2 \text{ (from curve)} &= 34^\circ.72, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{35.3453}{(139.283 + t)^{1.9154}},$$

which gives values in close agreement with the observed results.

Methyl Acetate. $\text{CH}_3\text{COOCH}_3$.

The sample boiled constantly at $57^\circ\cdot59$. Bar., 773·6 millims. Corrected and reduced b.p. = $57^\circ\cdot09$ ($57^\circ\cdot1$, Y. and T.).

The following are the observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
$0^\circ\cdot34$	101·53	·000057	·004761	$0^\circ\cdot34$	101·42	·000057	·004763
6·28	101·50	·000061	·004436	6·34	101·41	·000061	·004436
11·42	101·46	·000064	·004186	11·40	101·37	·000064	·004186
16·72	101·62	·000068	·003947	16·69	101·52	·000067	·003949
22·77	101·35	·000071	·003705	22·72	101·27	·000071	·003707
28·38	101·68	·000075	·003491	28·37	101·58	·000075	·003492
33·85	101·67	·000078	·003303	33·86	101·57	·000078	·003305
40·45	101·67	·000082	·003099	40·45	101·58	·000082	·003101
46·10	101·84	·000086	·002941	46·03	101·74	·000086	·002944
50·33	101·86	·000089	·002829	50·35	101·73	·000089	·002828
54·37	101·84	·000091	·002723	54·29	101·73	·000091	·002731

The value $d(0^\circ/4^\circ) = 0\cdot95932$, and the expression

$$V = 1 + \cdot0_2134982t + \cdot0_687098t^2 + \cdot0_735562t^3,$$

have been used in the reduction of the observations.

Taking

$$\begin{aligned} \eta_1 &= \cdot004762 & \eta_3 &= \cdot002727 & \eta_2 \text{ (calculated)} &= \cdot003604, \\ t_1 &= 0^\circ\cdot34 & t_3 &= 54^\circ\cdot33 & t_2 \text{ (from curve)} &= 25^\circ\cdot32, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{57\cdot4012}{(154\cdot499 + t)^{1\cdot8636}},$$

which gives results almost identical with those observed.

Ethyl Acetate. $\text{CH}_3\text{COOCH}_2\text{CH}_3$.

The boiling-point was constant at $77^\circ\cdot25$. Bar. 761·8 millims. Corrected and reduced b.p. = $77^\circ\cdot18$ ($77^\circ\cdot15$, Y. and T.).

The results of the viscosity observations are as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°24	100·50	·000045	·005767	0°26	100·42	·000045	·005759
8·90	100·47	·000050	·005146	8·89	100·38	·000050	·005142
14·50	100·07	·000053	·004789	14·43	100·10	·000053	·004802
21·38	100·24	·000057	·004413	21·37	100·25	·000057	·004424
28·14	99·86	·000061	·004093	28·11	99·83	·000061	·004099
36·58	100·11	·000066	·003734	36·50	100·08	·000066	·003742
44·12	99·81	·000070	·003452	44·12	99·77	·000070	·003459
51·18	100·39	·000075	·003224	51·12	100·30	·000075	·003224
60·18	100·38	·000080	·002960	60·15	100·32	·000080	·002960
68·50	100·41	·000085	·002737	68·37	100·33	·000085	·002746
74·61	100·50	·000089	·002593	74·58	100·42	·000089	·002595

In reducing the observations we have used $d(0^\circ/4^\circ) = 0.92436$, and the expression

$$V = 1 + 0.12185t + 0.45587t^2 - 0.576926t^3.$$

Taking

$$\begin{aligned} \eta_1 &= 0.05763 & \eta_3 &= 0.02594 & \eta_2 \text{ (calculated)} &= 0.03866, \\ t_1 &= 0^\circ.25 & t_3 &= 74^\circ.60 & t_2 \text{ (from curve)} &= 33^\circ.38, \end{aligned}$$

we obtain the formula

$$\eta = \frac{45.322}{(135.423 + t)^{1.8268}},$$

which satisfactorily reproduces the observed values.

Propyl Acetate. $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$.

The sample boiled between $101^\circ.93$ and $102^\circ.00$. Bar., 770.6 millims. Corrected and reduced b.p. = $101^\circ.52$ ($101^\circ.55$, Y. and T.).

Observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°39	101.04	·000034	·007349	0°38	101.03	·000034	·007674
9·78	100·95	·000039	·006645	9·79	100·87	·000039	·006673
20·59	100·81	·000044	·005757	20·59	100·79	·000044	·005768
30·15	100·86	·000049	·005102	30·11	100·81	·000049	·005115
39·76	100·93	·000054	·004562	39·75	100·86	·000054	·004564
50·37	100·98	·000060	·004064	49·71	100·89	·000059	·004097
61·37	101·00	·000066	·003621	61·35	100·93	·000066	·003628
69·90	101·01	·000071	·003328	69·89	100·92	·000071	·003334
80·03	100·97	·000076	·003027	79·98	100·90	·000076	·003030
89·50	100·99	·000082	·002775	89·50	100·90	·000082	·002775
96·97	100·99	·000086	·002604	96·84	100·91	·000086	·002600

The value 0.91016 for the density at 0°, and the expression

$$V = 1 + .0_2119136 t + .0_641636 t^2 + .0_7195991 t^3,$$

have been used in reducing the observations.

Taking

$$\begin{aligned} \eta_1 &= .007661 & \eta_3 &= .002602 & \eta_2 \text{ (calculated)} &= .004465, \\ t_1 &= 0^\circ.39 & t_3 &= 96^\circ.75 & t_2 \text{ (from curve)} &= 41^\circ.76, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{73.6005}{(125.269 + t)^{1.8972}},$$

which gives values in good agreement with those of observation.

Methyl Propionate. $\text{CH}_3\text{CH}_2\text{COOCH}_3$.

The boiling-point was constant at 79°.66. Bar., 759.1 millims. Corrected and reduced b.p. = 79°.70 (79°.67, Y. and T.).

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°.39	100.34	.000046	.005789	0°.37	100.25	.000046	.005787
9.73	100.33	.000051	.005139	9.73	100.25	.000051	.005145
16.81	100.26	.000055	.004719	16.77	100.22	.000055	.004731
23.70	100.27	.000059	.004363	23.21	100.21	.000059	.004372
29.61	100.23	.000062	.004096	29.62	100.13	.000062	.004100
38.67	100.23	.000067	.003746	38.65	100.14	.000067	.003746
45.58	100.22	.000071	.003472	45.60	100.12	.000071	.003481
52.64	100.54	.000075	.003253	52.67	99.82	.000075	.003256
60.38	100.39	.000080	.003027	60.37	100.33	.000080	.003029
68.55	100.39	.000085	.002807	68.43	100.30	.000084	.002816
75.86	100.40	.000089	.002638	73.84	100.31	.000089	.002636

We have used 0.9387 as the value of the density at 0°, and the expression

$$V = 1 + .0_213049 t + .0_513275 t^2 + .0_746943 t^3$$

in reducing the observations.

Taking

$$\begin{aligned} \eta_1 &= \cdot 005788 & \eta_3 &= \cdot 002677 & \eta_2 \text{ (calculated)} &= \cdot 003907, \\ t_1 &= 0^\circ\cdot 38 & t_3 &= 75^\circ\cdot 85 & t_2 \text{ (from curve)} &= 34^\circ\cdot 22, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{74\cdot 898}{(146\cdot 621 + t)^{1\cdot 89725}},$$

which gives values which agree closely with those observed.

Ethyl Propionate. $\text{CH}_3\cdot\text{CH}_2\cdot\text{COOCH}_2\cdot\text{CH}_3$.

The boiling-point varied between $98^\circ\cdot 95$ and $99^\circ\cdot 03$. Bar., 756·5 millims. Corrected and reduced b.p. = $99^\circ\cdot 14$ ($99^\circ\cdot 0$, Y. and T.).

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0·43	100·71	·000038	·006884	0·35	100·69	·000037	·006896
10·12	100·15	·000042	·006032	10·06	100·20	·000042	·006042
20·10	99·53	·000047	·005310	20·07	99·60	·000047	·006323
29·74	98·97	·000052	·004733	29·73	98·96	·000051	·004738
39·88	98·85	000057	·004226	39·87	98·81	·000057	·004235
49·64	98·69	·000062	·003818	49·72	98·70	·000062	·003817
59·12	99·91	·000068	·003477	59·16	99·82	·000068	·003478
69·23	99·87	·000074	·003148	69·24	99·78	·000074	·003162
72·12	99·55	·000075	·003072	72·12	99·50	·000075	·003075
80·04	99·50	·000079	·002855	80·25	99·45	·000079	·002854
89·68	99·50	·000085	·002627	89·70	99·42	·000085	·002627

In reducing the observations we have used 0·91240 for the density at 0° , and the expression

$$V = 1 + \cdot 0_2 119971 t + \cdot 0_5 14867 t^2 + \cdot 0_7 10599 t^3$$

for the thermal expansion.

Taking

$$\begin{aligned} \eta_1 &= \cdot 006890 & \eta_3 &= \cdot 004254 & \eta_2 \text{ (calculated)} &= \cdot 004254, \\ t_1 &= 0^\circ\cdot 39 & t_3 &= 89^\circ\cdot 69 & t_2 \text{ (from curve)} &= 39^\circ\cdot 38, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{72\cdot 981}{(133\cdot 905 + t)^{1\cdot 8914}},$$

which gives values in close concordance with those of observation.

Methyl Butyrate. $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOCH}_3$.

The sample distilled between $102^\circ\cdot65$ and $102^\circ\cdot67$. Bar., 758·8 millims. Corrected and reduced b.p. = $102^\circ\cdot67$ ($102^\circ\cdot75$, Y. and T.).

Observations on viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0·38	101·34	·000035	·007544	0·26	101·32	·000035	·007558
10·49	101·22	·000040	·006524	10·41	101·16	·000040	·006531
20·37	101·04	·000045	·005729	20·39	100·99	·000045	·005726
30·68	100·85	·000050	·005048	30·59	100·82	·000050	·005051
40·62	100·56	·000055	·004499	40·54	100·51	·000055	·004507
50·25	100·16	·000060	·004058	50·35	100·21	·000060	·004058
60·19	100·14	·000065	·003667	60·22	100·05	·000065	·003668
71·59	100·34	·000071	·003288	71·40	100·26	·000071	·003302
79·56	100·31	·000076	·003053	79·35	100·24	·000076	·003061
90·64	100·39	·000082	·002765	90·62	100·29	·000082	·002770
98·14	100·42	·000086	·002593	98·42	100·47	·000086	·002591

In reducing the observations, we have used $d(0^\circ/4^\circ) = 0\cdot92006$ for the density, and the expression

$$V = 1 + \cdot0_2113062\ t + \cdot0_524809\ t^2 + \cdot0_336230\ t^3$$

for the thermal expansion.

Taking

$$\begin{aligned} \eta_1 &= \cdot007551 & \eta_3 &= \cdot002597 & \eta_2 \text{ (calculated)} &= \cdot004428, \\ t_1 &= 0^\circ\cdot32 & t_3 &= 98^\circ\cdot03 & t_2 \text{ (from curve)} &= 42^\circ\cdot13, \end{aligned}$$

the formula

$$\eta_t = \frac{53\cdot0991}{(123\cdot745 + t)^{1\cdot8375}}$$

is obtained, which satisfactorily reproduces the observed values.

Methyl Isobutyrate. $(\text{CH}_3)_2\text{CH}.\text{COOCH}_3.$

The sample boiled between $92^\circ.03$ and $92^\circ.05$. Bar., 754.8 millims. Corrected and reduced b.p. = $92^\circ.26$ ($92^\circ.3$, Y. and T.).

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
$0^\circ.35$	100.06	.000039	.006682	$0^\circ.22$	100.08	.000039	.006696
9.48	99.97	.000043	.005904	9.32	99.89	.000043	.005925
18.12	99.91	.000047	.005297	18.11	99.82	.000047	.005301
28.99	101.36	.000054	.004660	28.97	101.26	.000054	.004660
35.82	101.16	.000057	.004314	35.80	101.19	.000057	.004320
44.70	100.99	.000062	.003928	44.63	101.04	.000062	.003937
52.56	100.91	.000066	.003626	52.54	100.84	.000066	.003636
62.64	101.23	.000072	.003289	62.81	100.74	.000072	.003289
76.20	101.25	.000077	.003035	76.24	101.18	.000077	.003038
79.78	101.19	.000082	.002814	79.76	101.11	.000082	.002812
88.83	101.22	.000087	.002587	88.86	101.13	.000087	.002590

The value 0.91131 for the density at 0° , and the expression

$$V = 1 + .0_212170 t + .0_638334 t^2 + .0_722582 t^3$$

have been used in reducing the observations.

Taking

$$\begin{aligned} \eta_1 &= .006689 & \eta_3 &= .002589 & \eta_2 \text{ (calculated)} &= .004161, \\ t_1 &= 0^\circ.33 & t_3 &= 88^\circ.84 & t_2 \text{ (from curve)} &= 39^\circ.20, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{98.0935}{(139.956 + t)^{1.9405}},$$

which gives values agreeing fairly well with the observed numbers.

ETHERS.

Methyl Propyl Ether. $\text{CH}_3.\text{O}.\text{CH}_2.\text{CH}_2.\text{CH}_3.$

A sample prepared from methyl iodide and sodium propylate was distilled from sodium wire, and the portion boiling between $39^\circ.20$ and $39^\circ.28$ was used in the observations. Bar., 762.5 millims. Corrected and reduced b.p. = $39^\circ.15$.

The following are the observations of viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°30	101·83	·000069	·003064	0°30	101·78	·000069	·063065
5·16	101·65	·000072	·002912	5·12	101·62	·000072	·002916
10·47	102·60	·000076	·002757	10·47	102·53	·000076	·002761
15·17	102·53	·000079	·002630	15·18	102·48	·000079	·002630
20·09	102·49	·000082	·002514	20·11	102·42	·000082	·002512
25·74	102·48	·000085	·002385	25·72	102·41	·000085	·002385
29·43	102·00	·000087	·002300	29·53	102·08	·000087	·002301
35·03	101·61	·000090	·002187	35·28	101·65	·000090	·002187

In reducing the observations, ZANDER's value, 0·7420 for the density at 0°, and his expression

$$V = 1 + \cdot 0_214406 t + \cdot 0_699286 t^2 + \cdot 0_758817 t^3$$

for the thermal expansion ('Annalen,' 243, 2), have been employed.

Taking

$$\begin{aligned} \eta_1 &= \cdot 003064 & \eta_3 &= \cdot 002187 & \eta_2 \text{ (calculated)} &= \cdot 002589, \\ t_1 &= 0^\circ 30 & t_3 &= 35^\circ 15 & t_2 \text{ (from curve)} &= 16^\circ 80, \end{aligned}$$

the formula

$$\eta_t = \frac{8.4251}{(146.862 + t)^{1.5863}}$$

is obtained, which satisfactorily reproduces the observed values.

Ethyl Propyl Ether. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$.

Prepared from ethyl iodide and sodium propylate and dried over sodium wire. The portions used for viscosity observations boiled from 62°·93 to 62°·98. Bar., 747·7 millims. Corrected and reduced b.p. = 63°·44.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°32	101·38	·000054	·003955	0°38	101·31	·000054	·003950
5·66	101·30	·000057	·003709	5·64	101·22	·000057	·003719
10·63	101·23	·000060	·003511	10·68	101·15	·000060	·003510
15·65	101·14	·000063	·003323	15·67	101·10	·000063	·003326
20·38	101·10	·000065	·003162	20·27	101·04	·000065	·003169
25·39	102·01	·000069	·003005	25·30	101·96	·000070	·003006
30·11	102·00	·000072	·002863	30·06	101·92	·000072	·002864
35·12	101·91	·000074	·002725	35·04	101·89	·000074	·002729
39·96	101·75	·000077	·002600	40·01	101·69	·000077	·002597
45·63	101·59	·000080	·002466	45·62	101·52	·000080	·002466
50·35	101·53	·000083	·002364	50·25	101·49	·000083	·002362
55·06	101·40	·000086	·002262	54·95	101·36	·000086	·002266
60·32	101·32	·000089	·002157	60·03	101·32	·000089	·002161

The value 0.7544 for the density at 0°, and the expression

$$V = 1 + 0.213116 t + 0.526162 t^2 + 0.715617 t^3,$$

given by DOBRINER ('Annalen,' 243, 4), have been employed in reducing the observations.

Taking

$$\begin{array}{lll} \eta_1 = 0.003953 & \eta_3 = 0.002159 & \eta_2 \text{ (calculated)} = 0.002921, \\ t_1 = 0^\circ.35 & t_3 = 60^\circ.18 & t_2 \text{ (from curve)} = 28^\circ.16, \end{array}$$

the formula

$$\eta = \frac{284.675}{(183.355 + t)^{2.1454}}$$

is obtained. The agreement between the observed and calculated values is remarkably close.



Prepared by KRAFFT's method, and submitted to repeated fractionation from sodium wire. The fraction used in the determinations of viscosity boiled between 89°·86 and 89°·90. Bar. 760·8 millims. Corrected and reduced b.p. = 89°·84.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0.53	101.92	0.000041	0.005359	0.64	101.91	0.000041	0.005359
8.62	101.76	0.000045	0.004821	8.53	101.77	0.000045	0.004831
16.96	101.35	0.000049	0.004355	16.94	101.30	0.000049	0.004362
24.66	101.29	0.000053	0.003980	24.65	101.26	0.000053	0.003990
32.44	101.12	0.000057	0.003653	32.47	101.06	0.000059	0.003656
40.46	102.27	0.000062	0.003359	40.48	102.31	0.000062	0.003361
48.03	101.93	0.000065	0.003113	48.10	101.86	0.000065	0.003115
56.15	101.86	0.000070	0.002877	56.14	101.82	0.000070	0.002876
64.18	101.71	0.000074	0.002662	64.14	101.69	0.000074	0.002667
72.48	101.35	0.000078	0.002468	72.70	101.32	0.000078	0.002470
81.53	101.23	0.000083	0.002280	81.42	101.19	0.000083	0.002288
88.00	101.25	0.000087	0.002154	88.03	101.17	0.000087	0.002154

The value $d(0^\circ/0^\circ) = 0.7633$ for the relative density, and the expression

$$V = 1 + 0.212132 t + 0.539318 t^2 - 0.713644 t^3,$$

obtained by ZANDER ('Annalen,' 214, 163), have been used in reducing the observations.

Taking

$$\begin{array}{lll} \eta_1 = \cdot 005359 & \eta_3 = \cdot 002154 & \eta_2 (\text{calculated}) = \cdot 003398, \\ t_1 = 0^\circ \cdot 58 & t_3 = 88^\circ \cdot 01 & t_2 (\text{from curve}) = 39^\circ \cdot 27, \end{array}$$

the formula

$$\eta = \frac{104 \cdot 068}{(148 \cdot 362 + t)^{1 \cdot 9754}}$$

is obtained, which gives values in good agreement with those observed.

Methyl Isobutyl Ether. $\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH} \cdot (\text{CH}_3)_2$.

Prepared from methyl iodide and sodium isobutylate and fractionated from sodium wire. In the case of this ether the process appeared to work more satisfactorily than in any of the others, the yield being almost quantitative. Two series of viscosity observations were made on this substance.

The fraction used in the first set boiled between $59^\circ \cdot 40$ and $59^\circ \cdot 43$; bar. 763·8 millims.; corrected and reduced b.p. = $59^\circ \cdot 26$. After the viscosity observations had been completed, this fraction was digested for two days with phosphoric oxide, and again distilled.

The corrected and reduced boiling-point was practically the same as before, viz., $59^\circ \cdot 29$. A second set of viscosity observations was then made with this liquid, and as the results were practically identical with those of the first set, the second only are given below. A combustion gave the following results:—

	Found.	Calculated.
Carbon	68·22	68·18
Hydrogen.	13·64	13·64

Observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0·37	102·83	·000057	·003797	0·36	102·78	·000057	·003797
7·00	102·76	·000061	·003524	6·85	102·75	·000061	·003528
14·54	102·66	·000065	·003247	14·48	102·61	·000065	·003245
21·31	102·65	·000069	·003021	21·40	102·58	·000069	·003023
28·92	102·47	·000073	·002796	28·86	102·42	·000073	·002804
35·98	102·31	·000077	·002619	35·98	102·28	·000077	·002620
42·50	102·26	·000081	·002461	42·60	102·19	·000081	·002455
49·64	102·22	·000085	·002309	49·86	102·15	·000085	·002302
55·24	102·10	·000088	·002193	55·21	102·06	·000088	·002192

As the thermal expansion of methyl isobutyl ether had not previously been determined, a series of measurements had to be made with the dilatometer, in order to obtain the data required for the reduction of the observations on viscosity. The apparatus and method employed were those described by THORPE ('Chem. Soc. Trans.,' vol. 63, p. 262, 1893).

The observations with the dilatometer gave :—

T.	Obs.	Calc.	T.	Obs.	Calc.
0.0	2126.98	2126.76	30.83	2219.52	2219.41
4.82	2140.45	2140.48	35.01	2232.90	2232.94
10.71	2157.43	2157.62	40.48	2250.96	2251.03
16.76	2175.55	2175.64	46.06	2269.89	2269.97
20.75	2187.78	2187.79	49.33	2281.33	2281.29
25.80	2203.56	2203.46	54.23	2298.63	2298.59

The observed values lead to the following formula :—

$$V = 2126.76 + 2.8216833 t + .00536623 t^2 + .00001901 t^3,$$

from which the calculated values are obtained.

Dividing by the first term and correcting for the expansion of glass, the formula for the absolute expansion is found to be

$$V_t = 1 + .0_2135624 t + .0_5256232 t^2 + .0_890132 t^3.$$

From this is calculated the following table giving the volumes of methyl isobutyl ether for every 10° between 0° and its boiling-point :—

T.	Vol.	Diff.	T.	Vol.	Diff.
0	100000		30	104324	759
5	100685	685	35	105099	775
10	101383	698	40	105893	794
15	102095	712	45	106704	811
20	102822	727	50	107534	830
25	103565	743	55	108384	850

The density at 0° was found to be 0.7507.

Taking

$$\begin{aligned} \eta_1 &= .003797 & \eta_3 &= .002192 & \eta_2 \text{ (calculated)} &= .002885, \\ t_1 &= 0^\circ.36 & t_3 &= 55^\circ.22 & t_2 \text{ (from curve)} &= 25^\circ.92, \end{aligned}$$

the formula

$$\eta = \frac{122.591}{(174.318 + t)^{2.0109}}$$

is obtained, which gives values agreeing well with those observed.

Ethyl Isobutyl Ether. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_3)_2$.

A sample prepared from ethyl iodide and sodium isobutylate was distilled from sodium wire, and the portion boiling between $80^\circ.74$ and $80^\circ.79$ was collected separately. Bar. 750.2 millims. Corrected and reduced b.p. = $81^\circ.18$.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
$^\circ$				$^\circ$			
0.36	103.68	.000046	.004800	0.36	103.69	.000046	.004807
7.34	103.26	.000049	.004396	7.34	103.29	.000049	.004399
15.13	101.98	.000053	.004001	15.07	101.96	.000053	.004006
21.61	101.58	.000056	.003708	21.80	101.58	.000056	.003711
28.22	101.58	.000060	.003449	28.06	101.31	.000060	.003458
35.41	101.39	.000064	.003200	35.38	101.36	.000064	.003200
41.80	100.87	.000067	.002992	41.72	100.82	.000067	.003000
48.94	104.00	.000073	.002793	49.00	103.97	.000073	.002790
56.97	102.39	.000076	.002613	56.01	102.34	.000076	.002617
63.18	102.25	.000080	.002439	63.16	102.11	.000080	.002441
70.69	102.16	.000084	.002277	70.64	102.11	.000084	.002282
77.43	102.04	.000088	.002147	77.53	102.01	.000088	.002148

As in the case of methyl isobutyl ether, determinations had to be made of the thermal expansion of this liquid.

The observations with the dilatometer gave :—

T.	Obs.	Calc.	T.	Obs.	Calc.
0.0	2126.13	2125.89	48.09	2267.85	2267.87
6.51	2143.50	2143.65	56.31	2295.19	2295.15
16.33	2171.10	2171.20	63.84	2320.91	2321.06
23.87	2193.00	2193.03	71.97	2350.27	2350.12
32.02	2217.41	2217.37	76.50	2366.82	2366.83
40.17	2242.52	2242.54			

The observed values lead to the formula :—

$$V = 2125.89 + 2.7009474 t + .00416124 t^2 + .00002225 t^3,$$

from which the calculated values are obtained.

Dividing by the first term, and correcting for the expansion of glass, the formula for the absolute expansion is found to be

$$V = 1 + \cdot 0_2129999 t + \cdot 0_5199488 t^2 + \cdot 0_7105254 t^3.$$

From this is calculated the following table, giving the volumes of ethyl isobutyl ether for every 5° between 0° and its boiling-point :—

T.	Vol.	Diff.	T.	Vol.	Diff.
0	100000		45	106350	763
5	100655	655	50	107130	783
10	101321	666	55	107929	799
15	101998	677	60	108745	816
20	102688	690	65	109582	837
25	103391	703	70	110438	856
30	104108	717	75	111316	878
35	104839	731	80	112216	900
40	105587	748			

A determination of the density at 0° gave 0.75445. This value and the above expression for the thermal expansion were used in reducing the observations for viscosity.

Taking

$$\begin{aligned} \eta_1 &= \cdot 004804 & \eta_3 &= \cdot 002147 & \eta_2 \text{ (calculated)} &= \cdot 003212, \\ t_1 &= 0^\circ \cdot 36 & t_3 &= 77^\circ \cdot 48 & t_2 \text{ (from curve)} &= 35^\circ \cdot 00, \end{aligned}$$

the formula

$$\eta_t = \frac{98.4046}{(152.69 + t)^{1.9733}}$$

is obtained, which gives values agreeing satisfactorily with the observed numbers.



In our previous communication we gave a series of values of the viscosity coefficients of a sample of isopentane lent to us by the late Professor SCHORLEMMER. The quantity of liquid was very small, and the boiling-point varied by nearly 3° during the distillation. For these reasons, and also from the fact that the sample was obtained from petroleum, we thought it advisable to make additional observations on the viscosity of this substance, and, if possible, on a product obtained from a different source.

We have been able to examine three different samples of isopentane made respectively from English, Scotch, and Irish fusel oil by direction of the Photometric

Standards Committee, in the laboratory of the Royal College of Science, by Mr. ALFRED GREEVES.

The English fusel oil was obtained from potato spirit, the Scotch from spirit prepared from a mixture of maize and barley, and the Irish from spirit made from barley alone. In each case the fusel oil was fractionated, and the portion boiling between 128° and 132° was used in the preparation of the isopentane.

The alcohol was converted into the iodide, which was washed with a solution of soda, then with water, and after drying over calcium chloride was carefully fractionated.

The iodide was reduced by means of a copper-zinc couple, and the mixture of isopentane and amylene thus produced was placed over excess of bromine for two days. The product was then separated from the bromine, washed with an ice-cold solution of soda, and then submitted to fractionation, which affords a ready method of separating the isopentane from amylene dibromide. As a further precaution against the presence of traces of amylene, amylene dibromide, or amyl iodide, the product was treated with fuming sulphuric acid for some hours. As this acid attacks isopentane to some extent, on removal from the acid the product was washed with dilute soda and then with water to remove sulphur dioxide; it was next dried over ordinary sulphuric acid for some days, then over sodium wire, and finally submitted to fractionation.

The observed boiling-points were :—

I.	From English amyl alcohol	. .	$28^{\circ}\cdot 17$ to $28^{\circ}\cdot 27$.	Bar., 765·9 millims.
II.	„ Scotch „ „	. .	$28^{\circ}\cdot 10$ to $28^{\circ}\cdot 12$.	„ 762·5 „
III.	„ Irish „ „	. .	$27^{\circ}\cdot 65$ to $27^{\circ}\cdot 70$.	„ 750·3 „

Corrected and reduced boiling-points :—

I.	II.	III.
$27^{\circ}\cdot 99$	$28^{\circ}\cdot 04$	$28^{\circ}\cdot 04$

These values are considerably lower than most of the published determinations of the boiling-point of isopentane. They are almost identical, however, with that recently found by YOUNG, and by YOUNG and THOMAS, viz., $27^{\circ}\cdot 95$ ('Proc. Phys. Soc.,' vol. 13, pp. 607 and 666, 1895).

Determinations of vapour density :—

	I.	II.	III.	
Found	36·05	35·78	35·55	
	35·61	35·62	35·63	Calculated, 35·83.

The following are the observations for viscosity :—

I.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°				0°			
0·45	99·68	·000064	·002785	0·44	99·61	·000064	·002782
5·16	99·60	·000066	·002651	5·15	99·55	·000066	·002644
10·82	99·57	·000069	·002514	10·85	99·50	·000069	·002491
15·33	99·53	·000072	·002393	15·34	99·48	·000072	·002383
20·29	99·51	·000074	·002282	20·22	99·47	·000075	·002275
25·16	99·53	·000077	·002174	25·15	99·48	·000077	·002170

II.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°				0°			
0·35	100·05	·000064	·002759	0·37	100·03	·000064	·002760
5·68	99·95	·000067	·002607	5·67	99·93	·000067	·002606
10·21	99·84	·000070	·002488	10·04	99·80	·000070	·002494
15·67	100·58	·000074	·002354	15·65	100·56	·000074	·002357
20·46	100·55	·000076	·002244	20·46	100·50	·000076	·002248
23·90	100·53	·000078	·002172	23·88	100·46	·000078	·002171

III.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°				0°			
0·31	101·18	·000065	·002767	0·35	101·14	·000065	·002765
5·62	101·11	·000068	·002612	5·60	101·05	·000068	·002607
10·90	101·03	·000071	·002471	10·94	100·97	·000071	·002472
16·02	100·84	·000074	·002357	15·97	100·83	·000073	·002361
19·87	100·73	·000076	·002262	19·88	100·69	·000076	·002268
23·44	100·68	·000078	·002185	23·49	100·64	·000078	·002193

In reducing the observations we have used Professor YOUNG's value, 0·6392 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 146834 t + \cdot 0_5 509626 t^2 + \cdot 0_8 6979 t^3,$$

given by THORPE and JONES (*loc. cit.*).

The comparison of the values given by these three samples with those given by the petroleum sample (A.) is contained in the following table.

In the case of each sample two curves were plotted, and the coefficients were read off at every 5°. The means of these values are given in the table, which also shows at each temperature-interval the differences between the coefficients of samples II., III., and A., and that of I.

Temp.	I.	II.		III.		A.	
	η .	η .	Difference.	η .	Difference.	η .	Difference.
0	·002797	·002769	·000028	·002776	·000021	·002726	·000071
5	·002651	·002624	·000027	·002627	·000024	·002583	·000068
10	·002521	·002494	·000027	·002495	·000026	·002456	·000065
15	·002398	·002371	·000027	·002375	·000023	·002340	·000058
20	·002283	·002255	·000028	·002264	·000019	·002233	·000050
25	·002175	·002149	·000026	·002158	·000017	·002130	·000045

The table shows that no two samples gave precisely the same values, No. I.—the isopentane derived from potato spirit, giving the largest, and A—the isopentane from petroleum, the smallest value.

The values given by No. I. are about 1·1 per cent. larger than those given by No. II., and 0·9 per cent. larger than those given by No. III., whilst they are 2·5 per cent. larger than those given by the petroleum hydrocarbon. It is evident, therefore, that the isopentane from petroleum was not a pure product, and further that on preparing the hydrocarbon from amyl alcohol in the manner just described, although the boiling-points and vapour-densities of the three samples are practically the same, yet, as regards their viscosities, slight differences can be detected, which can only be due to the difference in the origin of the samples.

Apparently, the lower the boiling-point and the higher the viscosity the more likely is it that the substance is pure; we, therefore, regard the values for η given by No. I. as nearest to the truth. It may be that isoamylene, which is less viscous than isopentane, may be present to some extent in Nos. II. and III.

In what follows we have used the coefficients given by No. I. sample.

Taking

$$\begin{aligned} \eta_1 &= \cdot002783 & \eta_3 &= \cdot002172 & \eta_2 \text{ (calculated)} &= \cdot002458, \\ t_1 &= 0^\circ\cdot44 & t_3 &= 25^\circ\cdot15 & t_2 \text{ (from curve)} &= 12^\circ\cdot50, \end{aligned}$$

we obtain the formula

$$\eta_t = \frac{391\cdot101}{(208\cdot6 + t)^{2\cdot2186}},$$

which gives numbers in close agreement with those observed.

Mean. temp.	η .		Difference.
	Observed (mean).	Calculated.	
0.44	.002783	.002783	000000
5.15	.002647	.002649	— .000002
10.83	.002502	.002499	+ .000003
15.33	.002388	.002389	— .000001
20.25	.002279	.002276	+ .000003
25.15	.002172	.002172	000000

The above coefficients are, on the average, only about 1.5 per cent. smaller than those found for normal pentane, whereas the numbers given by the original sample of isopentane were about 4 per cent. smaller.

On substituting the above for the original values, the relationships previously traced between the viscosity magnitudes of the paraffins are slightly altered. Since, however, all the lower paraffins we examined were prepared from petroleum, we do not at present propose to make the substitution, as the values already given probably express the relative effect of chemical nature more correctly than would be the case if the hydrocarbons were prepared partly by other methods. As regards the absolute value of the viscosity coefficients, there can be little doubt that the numbers afforded by the isopentane from amyl alcohol are to be preferred.

Ethyl Benzene. $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_3$.

The specimen of ethyl benzene previously examined was prepared by fractionating a sample obtained from KAHLBAUM, whereas its three isomers, the xylenes, were prepared for us by Dr. G. T. MOODY from the pure sodium salts of the corresponding sulphonic acids. As Dr. MOODY kindly placed at our disposal a quantity of ethyl benzene, also prepared from the sodium salt of its sulphonic acid, a substance crystallizing in beautiful plates and having the formula $\text{C}_6\text{H}_4\cdot\text{C}_2\text{H}_5\cdot\text{SO}_3\text{Na} + \frac{1}{2}\text{H}_2\text{O}$, we carried out a fresh series of viscosity observations.

On distilling from sodium wire, the boiling-point varied between $136^\circ.05$ and $136^\circ.10$. Bar., 764.3 millims. Corrected and reduced b.p. $135^\circ.86$.

The value given by the original sample was $135^\circ.92$.

The following are the viscosity observations :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η .	Temp.	Press.	Corr.	η .
0°				0°			
0·28	100·74	·000029	·008699	0·27	100·65	·000029	·008706
14·35	100·68	·000035	·007149	14·22	100·62	·000035	·007166
24·98	100·69	·000039	·006252	25·02	100·63	·000039	·006258
39·86	100·75	·000046	·005270	39·84	100·67	·000046	·005281
53·60	100·73	·000052	·004573	53·38	100·65	·000052	·004580
65·42	101·10	·000058	·004076	65·39	101·04	·000058	·004080
77·68	101·14	·000063	·003650	77·66	101·06	·000063	·003654
89·84	101·15	·000069	·003296	89·86	101·06	·000069	·003291
105·96	100·48	·000076	·002900	105·93	100·39	·000076	·002901
119·16	100·53	·000082	·002622	119·17	100·46	·000082	·002625
131·89	100·57	·000088	·002392	131·97	100·49	·000088	·002390

In reducing the observations we have used the value 0·8832 for the density at 0°, and for the thermal expansion the expression

$$V = 1 + \cdot 0_886172 t + \cdot 0_525344 t^2 - \cdot 0_818319 t^3,$$

given by WEGER ('Annalen,' vol. 221, p. 67).

On plotting the above values the coefficients (II.) contained in the third column of the following table were obtained. The second column gives the coefficients (I.) found from the original sample of ethyl benzene, and the differences between the two series of values are given in the last column.

Temp.	η .		Difference.
	I.	II.	
0	·00874	·00874	00000
10	·00758	·007575	·000005
20	·006665	·00665	·000015
30	·00592	·00590	·00002
40	·00529	·005265	·000025
50	·00477	·00474	·00003
60	·00432	·00429	·00003
70	·00394	·00391	·00003
80	·00360	·003575	·000025
90	·003305	·003285	·00002
100	·003045	·00303	·000015
110	·002815	·002805	·00001
120	·00262	·00261	·00001
130	·002435	·002425	·00001

At low temperatures the values are identical, and at high temperatures the new sample gives coefficients which are the lower by about 0·4 per cent. Between 30°

and 90° the differences reach a maximum, but never amount to more than 0.7 per cent. The conclusions based upon the coefficients η given by the original sample remain, therefore, unaltered, and we do not think it necessary to deduce a new formula of the Slotte type to reproduce the values given by sample No. 2; because, when the temperature range is so extended as 130° , the average difference between calculated and observed values is as great as the above differences between the coefficients of the two samples. The formula already given for ethylbenzene, although derived from the values for sample No. 1, may still be taken to give values as near the truth as it is possible to obtain by means of a formula of the Slotte type from the coefficients given by sample No. 2.

GRAPHICAL REPRESENTATION OF RESULTS.

The relative position of the viscosity-curves of different members of the series of esters and ethers is shown in the following figures. The ordinates are viscosity-coefficients multiplied by 10^5 , and the abscissæ are temperatures.

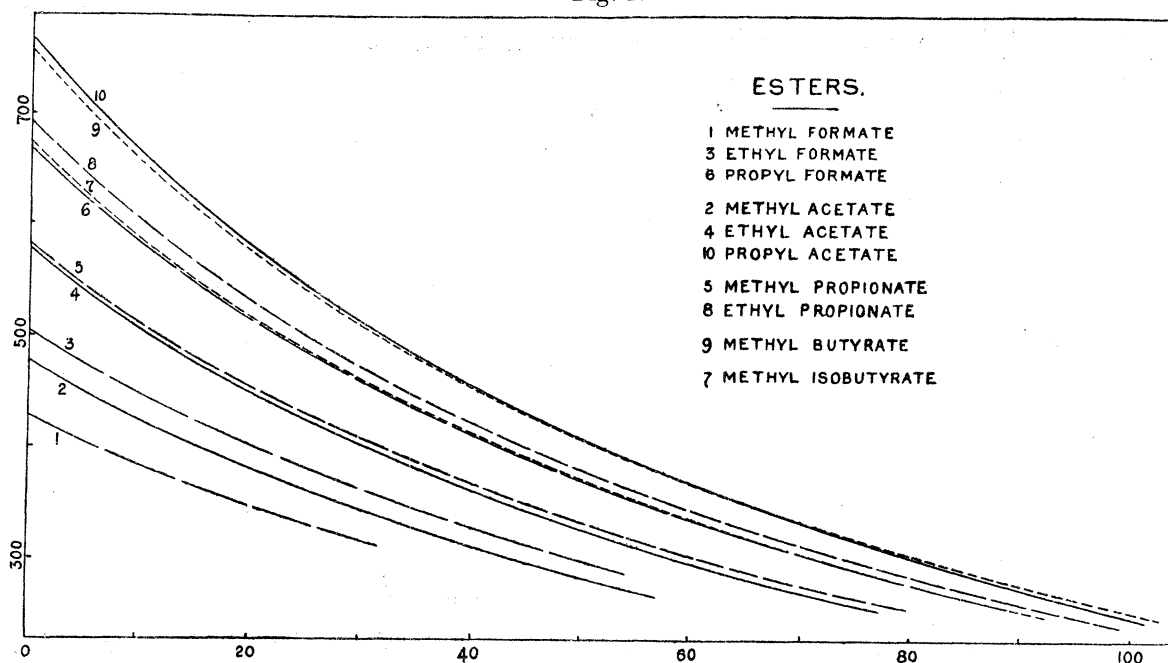
Esters (fig. 1).

The esters investigated were the three lowest formates, the three lowest acetates, the three lowest propionates, methyl butyrate, and methyl isobutyrate. Fig. 1 represents the curves obtained. The first noteworthy point in connection with the curves is, that in all cases their slope is comparatively small, and varies but little with the temperature. In this respect the esters differ to a most marked extent from the acids and alcohols from which they are derived, since one of the characteristic features of these two classes of compounds was the large effect exerted by temperature upon viscosity, and the large extent to which this effect altered as the temperature altered. The behaviour of the esters, therefore, is a further argument in support of our conclusion that the presence of the hydroxyl-group is the main cause of the exceptional course of the curves for the acids and alcohols, for it proves that when by the mutual interaction of an acid and alcohol the hydroxylic nature of both is destroyed, the resulting compound gives a curve in no way resembling those of the reacting substances. Indeed, the curves for the esters resemble in shape those of non-associated liquids in general; they give no indication of the presence of molecular aggregates. This is, of course, in harmony with the mass of physical evidence, which goes to show that, with very few exceptions, hydroxy-liquids alone contain molecular aggregates.

As regards the disposition of the curves, it has to be noted, in the first place, that according to the general rule obeyed in homologous series of simple liquids, they follow one another in the order of the molecular weights of the esters. Passing along the diagram from below upwards we have, first, the curve for methyl formate,

then the curves for its next higher homologues, the isomers methyl acetate and ethyl formate; then come the curves for the next higher homologues, the isomers ethyl acetate, methyl propionate, and propyl formate; and, lastly, the curves for the next higher isomeric homologues methyl isobutyrate, ethyl propionate, methyl butyrate, and propyl acetate. Passing to the relative position of the curves for isomeric esters, it is noticeable that, where the comparison is possible, the formate has at any temperature, the largest viscosity-coefficient. The curve for ethyl formate lies to the right of that for methyl formate, and the curve for propyl formate is far to the right of those for ethyl acetate and methyl propionate; indeed, at low temperatures it

Fig. 1.



almost coincides, and at high temperatures it actually coincides, with the curve of its higher homologue, methyl isobutyrate. It is more than likely that the large viscosity-coefficients of the formates are associated with the fact, previously established, that of the five lowest fatty acids, formic acid has, at low temperatures, the largest coefficients, and that these coefficients are larger than they might be expected to be even on making allowance for molecular aggregation.

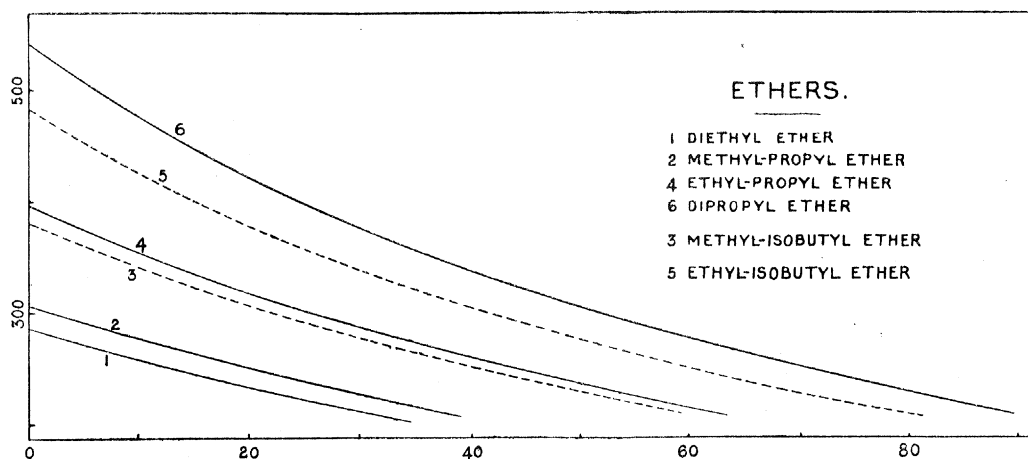
On comparing the isomeric propionates and acetates, it is seen that although the curve for ethyl acetate is very slightly to the left of that for methyl propionate, the curve for propyl acetate is far to the right of that for ethyl propionate. This is the result of the influence exerted by the symmetry of the molecule in lowering the viscosity. In the first case the acetate is a symmetrical compound and the propionate is unsymmetrical; in the second case both compounds are unsymmetrical. In conformity with the general rule, the curve for methyl isobutyrate lies well to the

left of that of methyl butyrate—it is, indeed, to the left of those of any of its isomers. The curves of methyl butyrate and propyl acetate are interesting inasmuch as, contrary to what holds in most series of related substances, they cut one another. At 0° the coefficient of the acetate is the larger by about 1·4 per cent., while at 100° the coefficient of the butyrate is the larger by about 2·4 per cent.

Ethers.

Five ethers have been dealt with in the previous part of this paper. The curves obtained are given in fig. 2, which also contains, for the sake of comparison, the curve for ethyl ether. As in the case of the esters, the effect of temperature on viscosity is small, and does not vary much as the temperature alters.

Fig. 2.



On passing along the diagram from below upwards the order of the curves is: diethyl ether, methyl propyl ether, methyl isobutyl ether, ethyl propyl ether, ethyl isobutyl ether, and dipropyl ether. They follow, therefore, in the order of the molecular weights of the compounds.

As regards the curves of isomers, it is noticeable that diethyl ether, the symmetrical isomer, has at all temperatures a lower viscosity than methyl propyl ether.

Again, as in the case of esters, of the isomeric ethers the iso-compound has the lowest viscosity; the curve for methyl isobutyl ether lies below that of ethyl propyl ether, and the curve for ethyl isobutyl ether lies below that of the symmetrical isomer dipropyl ether. This last comparison is interesting as showing that the presence of an iso-linkage has a more important effect in reducing the viscosity than the mere symmetry of the molecule.

In our previous paper an effect of symmetry similar to that which holds for the esters and ethers was shown by diethyl and methyl propyl ketones; the symmetrical isomer had the lowest viscosity.

The following tables contain the coefficients of viscosity read off from the working curves at intervals of 10°. Similar values for the new samples of isopentane and ethyl benzene have already been given on pp. 89 and 91 respectively.

COEFFICIENTS of Viscosity (Dynes per sq. centim.).

Esters.

Temp.	Methyl Formate.	Ethyl Formate.	Propyl Formate.	Methyl Acetate.	Ethyl Acetate.
°					
0	·00429	·00505	·00668	·00478	·00578
10	·00384	·00448	·00584	·00425	·00507
20	·00347	·00402	·00516	·00381	·00449
30	·00317	·00362	·00459	·00344	·00401
40	..	·00328	·00411	·00312	·00360
50	..	·002995	·00371	·00284	·00326
60	·003365	..	·002965
70	·003065	..	·00270
80	·00280		..

Temp.	Propyl Acetate.	Methyl Propionate.	Ethyl Propionate.	Methyl Butyrate.	Methyl Isobutyrate.
°					
0	·00770	·00582	·00693	·00759	·006725
10	·006655	·00512	·00604	·00657	·00587
20	·00581	·00454	·00532	·00575	·00518
30	·00511	·00408	·00472	·00508	·00461
40	·00455	·00368	·004225	·00453	·00413
50	·00408	·00334	·003805	·00407	·00372
60	·003675	·00304	·00345	·003675	·003375
70	·003335	·002775	·003135	·00334	·00307
80	·003035	..	·00286	·00304	·00280
90	·00276	..	·00262	·00278	·00256
100	·00250	·00256	..

Ethers.

Temp.	Methyl Propyl Ether.	Ethyl Propyl Ether.	Dipropyl Ether.	Methyl Isobutyl Ether	Ethyl Isobutyl Ether.
°					
0	·00307	·003965	·00540	·00381	·00482
10	·00277	·00354	·00474	·00340	·00425
20	·002515	·003175	·00420	·003065	·003785
30	·00228	·002865	·00375	·00277	·00339
40	..	·00260	·003375	·00252	·003045
50	..	·00237	·003045	·00230	·002765
60	..	·002165	·00277	..	·00251
70	·00252	..	·00229
80	·00231	..	·002105

Conclusions relating to the Graphical Representation of the Results.

Both ethers and esters give no evidence of molecular aggregation and conform to the rules that—

- (1.) In homologous series the viscosity is greater the greater the molecular weight.
- (2.) An iso-compound has a smaller viscosity than a normal isomer.
- (3.) The more symmetrical the molecule of an isomeric compound the lower is the viscosity.

As regards the esters themselves it is noteworthy, where the comparison has been made, that—

- (4.) Of isomeric esters the formate has the largest viscosity.

ALGEBRAICAL REPRESENTATION OF THE RESULTS.

The following table gives the values of the constants in SLOTTE's formula for the esters and ethers. Here the formula is written in the shape $\eta = C/(1 + bt)^n$ instead of that already used, viz., $\eta = C/(\alpha + t)^n$. C is, of course, the value of η at 0° , and since, in general, the curves do not cross one another, relationships exist between the values of C for the different substances similar to those just discussed and which hold regarding the position of the viscosity curves.

CONSTANTS in SLOTTE's formula $\eta = C/(1 + bt)^n$.

	C.	b.	n.
Methyl formate. . . .	·004301	·014655	0·8325
Ethyl formate	·005048	·007197	1·7006
Propyl formate	·006679	·007179	1·9154
Methyl acetate	·004781	·006472	1·8636
Ethyl acetate	·005783	·007384	1·8268
Propyl acetate	·007706	·007983	1·8972
Methyl propionate. . .	·005816	·006820	1·8972
Ethyl propionate . . .	·006928	·007468	1·8914
Methyl butyrate	·007587	·008081	1·8375
Methyl isobutyrate . .	·006720	·007144	1·9405
Diethyl ether	·002864	·007332	1·4644
Methyl propyl ether . .	·003077	·006809	1·5863
Ethyl propyl ether . .	·003969	·005454	2·1454
Dipropyl ether	·005401	·006740	1·9734
Methyl isobutyl ether .	·003813	·005737	2·0109
Ethyl isobutyl ether . .	·004826	·006549	1·9733

Since the values of n and b are interdependent, their individual magnitudes need not show any definite relationships to the chemical nature of the substances. It is easy to prove, however, by the method already adopted, that the temperature

coefficients are in reality closely related to chemical nature. If the denominator of the left-hand side of the equation $\eta = C/(1 + bt)^n$ be expanded, and if terms involving higher powers of t than t^2 be neglected, we obtain an expression of the shape $\eta = C/(1 + \beta t + \gamma t^2)$. Such an expression closely reproduces the observed values of esters and ethers. This is shown in the following table, which also gives the values of β and γ .

$$\text{FORMULA } \eta = C(1 + \beta t + \gamma t^2).$$

	β .	γ .	t .	$\eta \times 10^5$ (Calc.).	$\eta \times 10^5$ (Obs.).	Diff. $\times 10^5$.
Methyl formate	·01220	—0·1497	30	318	317	—1
Ethyl formate	·01224	0·3086	50	299	299	0
Propyl formate	·01375	0·4519	80	280	280	0
Methyl acetate	·01206	0·3370	50	283	284	1
Ethyl acetate	·01349	0·4117	70	269	270	1
Propyl acetate	·01514	0·5423	100	252	250	—2
Methyl propionate	·01294	0·3958	70	277	277	0
Ethyl propionate	·01412	0·4701	90	261	261	0
Methyl butyrate	·01485	0·5025	100	254	256	2
Methyl isobutyrate	·01386	0·4657	90	256	256	0
Diethyl ether	·01074	0·1828	30	214	212	—2
Methyl propyl ether	·01080	0·2156	30	229	228	—1
Ethyl propyl ether	·01170	0·3655	60	216	216	0
Dipropyl ether	·01330	0·4363	80	231	231	0
Methyl isobutyl ether	·01154	0·3345	50	230	230	0
Ethyl isobutyl ether	·01292	0·4119	80	209	210	1

The last four columns in the table go to show that even at high temperatures where, from its mode of derivation the formula should be least satisfactory, it gives values agreeing closely with those observed. Under t is given a temperature near the boiling-point of the liquid; under (calc.) and (obs.), the calculated and observed values, respectively, of the viscosity-coefficients at t , and the difference between the values is given in the last column. It is clear that in all cases a formula of the above type will closely reproduce the observed values of η , and, consequently, β and γ may be regarded as the temperature-coefficients of the different substances. It will be seen from the table that the magnitudes of β and γ are closely related to chemical composition. From the fact that the value of n for methyl formate happens to be less than unity, the value of γ for this ester is negative, and hence its coefficients cannot be satisfactorily compared with those of the other substances, as they are all positive. Excluding methyl formate, the table shows that in general—

- (1.) In any homologous series β and γ increase as the molecular weight increases.
- (2.) Of isomeric compounds the iso-compound has the smallest coefficients.
- (3.) Ethyl ether, the symmetrical isomer, has smaller coefficients than methyl propyl ether.

(4.) As regards normal isomeric esters, the formate has the largest and the propionate the smallest coefficients, and the values of the acetate are larger than of the butyrate.

COMPARISON OF VISCOSITY MAGNITUDES AT COMPARABLE TEMPERATURES.

In what follows we deal with the relationships which exist between the various viscosity magnitudes—the viscosity-coefficient, the molecular viscosity, and the molecular viscosity work—first, at the boiling-point, and, second, at temperatures of equal slope, the slope adopted being that employed in our previous paper, viz., 0.0_{4323} .

A. COMPARISON of Viscosity Magnitudes at the Boiling-point.

Esters.

	Viscosity-Coefficients. η in dynes per sq. centim. $\times 10^5$.			Molecular Viscosity. η in dynes per sq. centim. \times specific molecular area in sq. centims. $\times 10^4$.			Molecular Viscosity Work. η in dynes per sq. centim. \times specific molecular vol. in cub. centims. $\times 10^3$.		
	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.
Formate . .	312	289	278	492	555	620	195	243	293
Acetate . .	266	253	246	508	567	626	222	268	315
Propionate .	255	242	..	565	614	..	266	309	..
Butyrate . .	250	630	317
Isobutyrate .	251	633	318

Ethers.

	Viscosity-Coefficients. η in dynes per sq. centim. $\times 10^5$.	Molecular Viscosity. η in dynes per sq. centim. \times specific molecular area in sq. centims. $\times 10^4$.	Molecular Viscosity Work. η in dynes per sq. centim. \times specific molecular vol. in cub. centim. $\times 10^3$.
Methyl propyl .	211	471	222
Ethyl propyl . .	210	534	269
Dipropyl . . .	212	601	320
Diethyl . . .	205	459	217
Methyl isobutyl	210	534	269
Ethyl isobutyl .	208	593	316

As regards the esters, it will be seen that the different series follow the rule obeyed in most homologous series, viz., that the viscosity-coefficients diminish as the molecular weight increases. All the differences are negative, and diminish as a series is ascended.

Of the isomeric butyrates the iso-compound, in conformity with the general rule (compare p. 599, Part I.), has the larger coefficient. The ethers, however, afford an additional instance of an homologous series (compare pp. 590 and 592, Part I.) in which the different members have nearly the same viscosity at the boiling-point. On comparing the values for diethyl ether and methyl propyl ether the symmetrical compound, as in the case of the ketones (compare pp. 599 and 605, Part I.) has the lower viscosity.

The exceptional character of the formates is no doubt connected with the exceptional behaviour of formic acid, the molecular viscosity of which is abnormally large, greater, indeed, than that of acetic acid (compare pp. 591 and 610, Part I.).

In our previous paper we showed that the values of CH_2 varied in different series, but that on making allowance for the influence of molecular complexity and of differences in chemical constitution (compare p. 606, Part I.), we concluded that the probable value of the effect of CH_2 on the molecular viscosity of comparable liquids was 62. It is satisfactory to find that this number is almost identical with the mean value now given by the esters and ethers, as derived from the thirteen available differences, viz., 61 ± 6 .

As regards molecular viscosity work it will be seen that the differences between the formates and acetates are nearly constant and in mean about 25; whilst the remaining differences given by the esters are also fairly uniform, viz., 46, the mean value given by the ethers is 50. The general mean, 48 ± 3 , corresponds with that arrived at in our former paper, viz., 47.

The Value of Ether Oxygen.—Since the effect of CH_2 on the molecular viscosity and molecular viscosity work of the esters and ethers is the same as the value adopted in our previous paper, we may assume that the values of the atomic constants of carbon and hydrogen there used also apply in the case of the esters and ethers. If we further assume that the value of carbonyl oxygen is the same for the ethers as for the ketones, we have all the data for calculating the value of ether oxygens. The results are given in the following tables:—

Esters.

	$\text{C}_n\text{H}_{2n}\overset{\parallel}{\text{O}}\text{O}<.$ ηd^2 (Obs.).	$\text{C}_n\text{H}_{2n}\overset{\parallel}{\text{O}}.$ (Calc.).	$\text{O}<.$
Methyl formate	492	372	120
Ethyl formate	555	434	121
Propyl formate	620	496	124
Methyl acetate	508	434	74
Ethyl acetate	567	496	71
Propyl acetate	626	558	68
Methyl propionate	565	496	69
Ethyl propionate	614	558	56
Methyl butyrate	630	558	72
Methyl isobutyrate	633	573	60

Ethers.

	$\frac{C_n H_{2n+2} O <}{\eta d^2}$ (Obs.).	$\frac{C_n H_{2n+2} \cdot}{}$ (Calc.).	$O <.$
Diethyl	459	408	51
Methyl propyl	471	409	63
Ethyl propyl	534	470	61
Dipropyl	601	532	69
Methyl isobutyl	534	485	49
Ethyl isobutyl	593	547	46

As regards both molecular viscosity and molecular viscosity work, the formates—as was to be expected from what has been already stated—give values which are much larger than those of other compounds. Of the remaining liquids the general mean of the values of ethers and esters as regards molecular viscosity is 62 ± 8 . The variations of the individual values are no doubt large, arising mainly from the fact that in the case of normal isomers the same calculated value is deducted from the observed numbers, no regard being paid to the effect of symmetry of the molecule, etc., on the viscosity. A quantitative measure of these effects will only be possible after a much larger number of compounds has been investigated. There can, however, be no question of the large differences which exist between the atomic constants of hydroxyl oxygen, carbonyl oxygen, and ether oxygen.

Taking the value found above, we may now write as the probable values of oxygen in the three different conditions—

	Molecular Viscosity.	Molecular Viscosity Work.
Hydroxyl oxygen	196	102
Carbonyl oxygen	248	41
Ether oxygen	62	37

These numbers, of course, can only be regarded as provisional; they are mainly put forward as confirming the conclusion already indicated in our previous paper, that the constitution of oxy-compounds largely affects their viscosity.

B. COMPARISON OF VISCOSITY MAGNITUDES AT TEMPERATURES OF EQUAL SLOPE.

Esters.

	Viscosity-Coefficients. η in dynes per sq. cm. $\times 10^5$.			Molecular Viscosity. η in dynes per sq. cm. \times specific mol. area, in sq. cm. $\times 10^4$.			Molec. Viscosity Work. η in dynes per sq. cm. \times specific mol. vol., in cb.c. $\times 10^3$.		
	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.
Formate	345	336	336	538	635	734	212	276	344
Acetate	328	327	333	613	713	822	265	333	408
Propionate	334	336	..	720	822	..	334	407	..
Butyrate	338	826	408
Isobutyrate	335	819	405

Ethers.

	Viscosity-Coefficients. η in dynes per sq. cm. $\times 10^5$.			Molecular Viscosity. η in dynes per sq. cm. \times specific mol. area, in sq. cm. $\times 10^4$.			Molec. Viscosity Work. η in dynes per sq. cm. \times specific mol. vol., in cb.c. $\times 10^3$.		
	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.	Methyl.	Ethyl.	Propyl.
Methyl propyl.		302			648			300	
Ethyl propyl		310			755			373	
Dipropyl		318			865			451	
Diethyl		295			635			295	
Methyl isobutyl		311			757			374	
Ethyl isobutyl		312			849			444	

It will be seen, in the case of both esters and ethers, that the viscosity-coefficients at temperatures of equal slope are fairly concordant amongst themselves, and tend, in the case of the ethers, to become larger with increase of molecular weight. In the case of the ethers—diethyl and methyl propyl—the symmetrical compound, under all conditions of comparison, has the smaller value; in this respect the ethers resemble the ketones.

As in the case of the comparisons at the boiling-point, the formate has a larger molecular viscosity than any of the isomers (compare ethyl formate and methyl acetate; propyl formate and ethyl acetate)—another indication of the specific influence exerted by the formyl group. The values of other normal esters obey the rule that the more nearly the number of carbon atoms in the acid radicle approximates to the number in the alcohol radicle the lower is the molecular viscosity. Methyl isobutyrate gives a smaller value than methyl butyrate; a similar result was found in the case of six comparisons in our previous paper.

In any group of normal isomeric esters, the formate has the largest value of molecular viscosity work (compare ethyl formate with methyl acetate; propyl formate with ethyl acetate). The other members of the group have values which are practically identical (ethyl acetate 333, methyl propionate 334; propyl acetate 408, ethyl propionate 407, methyl butyrate 408. Methyl isobutyrate follows the general rule in giving a smaller value than the methyl butyrate.

Values for ether oxygen at temperatures of equal slope have been calculated using the values given in our previous paper for CH_2 and carbonyl oxygen, but it is evident that the values afforded by the esters are not independent of molecular weight, as they diminish, without exception, as any series of esters is ascended. Moreover, it is not possible to allow for the fact already noted that the molecular viscosity of an isomeric ester is the smaller the more nearly the number of carbon atoms in the acid radicle approximates to the number in the alcohol radicle. The main result, however, comes out as clearly as in the first condition of comparison that ether oxygen has invariably an effect on molecular viscosity widely different from the effects of hydroxyl oxygen and carbonyl oxygen. Thus, in the case of molecular viscosity, the values obtained were—

Hydroxyl oxygen	166
Carbonyl oxygen	198
Ether oxygen	51

Although these numbers can only be considered as first approximations, they clearly indicate, as already stated, that the constitution of oxy-compounds profoundly affects their viscosity.

The following table shows the temperature at which the viscosity curves have the slope $\cdot 0_4323$:—

Esters.

	Methyl.	Ethyl.	Propyl.
Formate	20°7	37°7	60°1
Acetate	34°7	49°6	69°9
Propionate	49°7	62°6	..
Butyrate	68°5
Isobutyrate	60°7

Ethers.

Methyl propyl	1°6
Ethyl propyl	22°4
Dipropyl	45°8
Diethyl	—2°7
Methyl isobutyl	18°7
Ethyl isobutyl	37°8

It will be noticed that in all cases an increment of CH_2 brings about an increase in the temperature of equal slope, and in all cases the increase becomes greater as the series is ascended. In any group of normal isomers the formate has the largest temperature value and, with the possible exception of ethyl propionate, the remaining esters in the group have almost the same value. According to the general rule, methyl isobutyrate has a lower value than methyl butyrate, and, as in the case of the ketones, of the two ethers, diethyl and methyl propyl, the symmetrical isomer has the lower equal-slope temperature.

APPENDIX.

On the Preparation of Ethers. By R. E. BARNETT, B.Sc., Assoc. R.C.S.

The ethers prepared and used for viscosity observations were methyl propyl, ethyl propyl, dipropyl, methyl isobutyl, and ethyl isobutyl.

The most rapid and economical method of preparing certain ethers is undoubtedly the "continuous etherification" of alcohols by means of sulphuric acid, first used by BOULLAY and investigated by WILLIAMSON. Although it has been shown, originally by WILLIAMSON ('Annalen,' 81, 77) and later by NORTON and PRESCOTT ('Amer. Chem. Journ.,' 6, 241), that this method is applicable to the preparation of mixed ethers, there are always formed, as would be expected, considerable quantities of the two possible simple ethers containing the same alkyl radicles. The great difficulty of separating any one ether from such a mixture, and the absence of any certain chemical method of ascertaining the presence of isomers, render this method particularly unsuitable for preparing ethers for physical investigation. The liability of the higher fatty alcohols to oxidation by the sulphuric acid, which limits the application of this method to alcohols containing not more than three carbon atoms (NORTON and PRESCOTT, *loc. cit.*), is partially obviated by the employment of the sulphonic acids of benzene, naphthalene, and similar compounds (KRAFFT, 'Berichte,' 26, 2829).

Although it is evident that the *à priori* objections mentioned above apply equally to this method, it was tried in preparing dipropyl ether. Employing benzenesulphonic acid, a liberal supply of which we owe to the kindness of Messrs. BROOKE, SIMPSON, and SPILLER, considerable difficulty was found in getting anything like complete etherification. Much propyl alcohol always came over with the ether, and as their boiling-points only differ by some seven degrees, the mixture was difficult to separate by fractionation. A better result was obtained by passing the first product through the acid again, but still much alcohol was present. After a rough separation, the ether was repeatedly treated with sodium wire, until further action practically ceased. The resulting product was fractionated four times in a LEBEL-HENNINGER apparatus. It was evidently a mixture, containing presumably also di-isopropyl and

propyl isopropyl ethers. The total range of boiling-point was from 85° to 90° (uncor.), while the boiling-point of dipropyl ether is $90^{\circ}\cdot 7$ (ZANDER, 'Annalen,' 214, 163). This product showed, as far as distillation can show, the presence of far greater proportions of isomeric compounds than the mixed ethers prepared from the same propyl alcohol in the manner presently to be described; this appears to confirm the view expressed above of the tendency to the formation of mixed ethers in these processes, and the consequent augmentation of the proportions of isomeric compounds present in the alcohol employed. The preparation of di-isobutyl ether by this process was also attempted by using naphthalene sulphonic acid, but the difficulty of complete etherification and the very impure product formed caused the process to be abandoned.

Excluding the method depending upon the action of silver oxide upon alkyl iodides (ERLENMEYER, 'Annalen,' 126, 306; LINNEMANN, 'Annalen,' 161, 37), the only other available processes are those based upon the condensation of alcohol with alkyl halides in the presence of an alcoholate or hydroxide of an alkyl metal, or of triethylamine. The last-named substance was employed by REBOUL ('Compt. Rend.,' 93, 69). As his method involves the use of sealed tubes, and does not prevent the formation of olefine, it was not tried.

The method described by CHANCEL ('Compt. Rend.,' vol. 68, p. 726; 'Annalen,' vol. 151, p. 305), and previously used by BALARD, has the advantage of dispensing with metallic sodium, and has consequently been frequently employed. CHANCEL prepared methyl, ethyl, propyl, and amyl propyl ethers by acting upon a mixture of propyl alcohol and powdered caustic potash with the alkyl iodide. The formation of the dipropyl ether, which is the only one fully described, was attended with the production of much propylene, especially in the presence of excess of alkali. The boiling-points given are so widely different from those of DOBRINER and other subsequent investigators that CHANCEL's ethers must have been very impure, probably from the presence of undecomposed iodide. LIEBEN and ROSSI ('Annalen,' vol. 158, p. 167) tried CHANCEL's process, using butyl iodide with caustic potash and ethyl alcohol, and found that two-thirds of the iodide was converted into ethyl-butyl ether. SAYTZEW ('Journ Prakt. Chem.,' (2), vol. 3, p. 88), using the same substances and a similar method obtained an amount of butylene representing about one-fourth of the iodide employed. MARKOWNIKOFF ('Annalen,' vol. 138, p. 374), obtained ethyl isopropyl ether as a bye-product in the action of potassium cyanide in alcoholic solution upon isopropyl iodide. He observed that the amount of ether produced increased with the strength of alcohol employed, reaching the maximum with absolute alcohol.

In trying this method, roughly-powdered caustic potash was added to propyl alcohol in a flask, and after cooling, ethyl iodide was poured in. The mixture was warmed on a water-bath under a reflux condenser; the action rapidly became very vigorous, and a considerable quantity of gas was evolved. After some time, when the reaction appeared to be complete, the liquid portion was distilled off and treated

with calcium chloride. It boiled entirely between 63° and 68° . On treatment with sodium it became evident that this product contained a very large quantity of undecomposed ethyl iodide, and it was found practically impossible to purify it by any means short of further etherification. In a second experiment more alkali was used, and in this case the mixture of propyl alcohol and caustic potash was kept hot, and ethyl iodide added through the reflux condenser at intervals. Gas was still given off, and the product obtained again boiled between the same limits and contained much iodide.

It will be seen that the disadvantage of CHANCEL'S method is that the large quantity of caustic alkali converts much of the alkyl iodide into olefine, while, on the other hand, unless a great excess of potash is used, the product contains undecomposed iodide.

Although an alcoholic solution of caustic alkali is stated to contain a large proportion of alcoholate, yet the other method, in which the alkali metal is dissolved in the pure alcohol, differs very markedly from CHANCEL'S, and, as will be seen from the experiments presently to be described, is greatly superior as a quantitative method for the preparation of ethers. This does not, however, immediately appear from the existing records. BRÜHL ('Annalen,' vol. 200, p. 177) acted upon sodium ethoxide in alcoholic solution with propyl bromide; he found propylene evolved, and the yield of ether low. ZANDER ('Annalen,' vol. 214, p. 163) employing sodium propylate with propyl iodide, obtained only a 25 per cent. yield of dipropyl ether. By the use of solid sodium ethoxide and butyl bromide, LIEBEN and ROSSI obtained ethyl butyl ether as chief product, with a small quantity of butylene; but this experiment was performed in a sealed tube and is consequently not quite comparable. It is noteworthy, however, that only 1.5 times the theoretical quantity of the ethoxide was used, while to decompose the less stable butyl iodide SAYTZEW (*loc. cit.*) had to use six times the calculated amount of potassium hydroxide in CHANCEL'S process.

A careful comparison of all the above-mentioned results with others by BALARD, GUTHRIE, and WILLIAMSON, has led, in the light of experiments described below, to conclusions which may be stated as follows; they refer to the preparation of ethers containing alkyl radicles from methyl to amyl inclusive.

i. The action of a solution of sodium in an anhydrous alcohol upon an alkyl halide tends quantitatively to the production of an ether,* and differs markedly from the action of an alcoholic solution of an alkaline hydroxide.

ii. In preparing mixed ethers by this reaction, the halogen-derivative should contain the alkyl radicle of lower molecular weight, the reaction then being apparently the more simple and regular, and the yield better the greater the difference between the two alkyls.

iii. Where the use of the halogen-derivative of propyl or a higher alkyl becomes

* Cf. HECHT and CONRAD ('Zeits. Physik. Chem.,' 3, 450), on this reaction.

unavoidable, the bromide, or sometimes the chloride, should be substituted for the iodide.

The second of these conclusions finds some support in the work of SILVA ('Compt. Rend.,' 81, 323), who showed that when a mixed ether is decomposed by hydriodic acid the higher radicle becomes an alcohol and the lower an iodide.

Although the rule given may seem obvious in view of the known instability of the higher alkyl iodides, it is shown above that in practice it has been generally disregarded. A possible reason for this is the increasing difficulty of dissolving sodium as we ascend the series of alcohols. In the work recorded below, it was not found possible in any reasonable time to dissolve more than one molecular proportion of sodium in two or three of propyl or isobutyl alcohols. The consequent waste of alcohol may be obviated by the use of the following continuous process, by means of which the conversion of alkyl iodides and alcoholates into ether can be carried out in almost theoretical proportions.

A WURTZ flask of about a litre capacity has the side-tube (which should be nearly at right angles to the neck) lengthened to about a metre, and this surrounded by the outer tube of a condenser for nearly its whole length to secure efficient condensation. The flask is placed on a water-bath, and by inclining it until the condenser slopes upward at some 30° with the horizontal we have a reflux apparatus, while a simple rotation through 60° downwards adapts it for distillation.

Placing it with the condenser sloping upwards, 150 grams of the alcohol (propyl or isobutyl) is introduced through the neck, which is fitted with an easily-removable cork. A clean dry bottle, wide mouthed and stoppered, is tared, and about 30 grams of clean sodium put into it. It is again weighed, so that at any time the amount used can be ascertained; if dry and well-stoppered, oxidation is only superficial. Some pieces are cut off and introduced into the flask; it dissolves rapidly at first with evolution of heat. More sodium is added at intervals, taking care not to use more than can be dissolved within a reasonable time; say 20 to 22 grams for 150 grams alcohol. The water-bath is heated, as if the solution be allowed to cool it solidifies. Directly the sodium has dissolved, the cork in the neck is replaced by one carrying a bent tap-funnel, in which the iodide (methyl or ethyl) is placed. This is allowed to flow in small portions into the thick liquid; the flask is gently rotated to prevent the heavy iodide sinking to the bottom and causing violent bumping, and in a moment the whole mass becomes clouded by the separation of sodium iodide. The whole of the iodide is gradually added in this way, the amount being that calculated for three-fourths of the sodium present. With this proportion, though but little more than equimolecular, there was never a trace of iodide in any of the distillates.

After a short digestion the condenser is turned down without interrupting the boiling, and the ether distils over. It is accompanied with but little alcohol, possibly on account of the alcoholate still in solution raising the boiling-point. Directly the

distillation slackens, the condenser is turned up again, and more sodium introduced ; a further quantity of ten or twelve grams can be dissolved in the remaining alcohol. An amount of alkyl iodide, three-fourths of that required for the total quantity of sodium alcoholate now in the flask, is added as before, and so a second quantity of ether obtained. It is possible to continue this process so that the final amounts of sodium and alcohol unutilised shall bear as small a proportion to the total ether produced as we please, especially if the alcohol obtained by fractionation of the early distillates be added to the flask ; but time and the accumulation of sodium iodide fix a practical limit.

The ethers prepared in this way were methyl-propyl, ethyl-propyl, methyl-isobutyl, and ethyl-isobutyl. The dipropyl ether was prepared by KRAFFT's method, as already described. The methyl and ethyl iodides used were prepared by myself. The alcohols were obtained from KAHLBAUM ; the propyl alcohol boiled between $95^{\circ}7$ and $97^{\circ}0$ (corr.), and the isobutyl alcohol from $106^{\circ}4$ to 108° (corr.). Each ether was repeatedly fractionated in a LEBEL-HENNINGER apparatus, and the main fraction, after frequent and prolonged digestion with sodium wire, boiled within about half a degree. It appeared to be practically impossible to obtain an ether which would show absolutely no gas bubbles on the introduction of fresh sodium wire, so one was compelled to consider the drying complete when the amount of this trifling action became constant on each successive addition of wire. This minute quantity of moisture would appear to have no effect upon the viscosity observations, as an ether after repeated treatment with phosphoric oxide gave results almost identical with those given by the liquid before treatment. (See p. 83.)