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Chemistry. — "The Temperature-coefficients of the free Surface-energy of Liquids, at Temperatures from —80° to 1650° C.:

IV. Measurements of some Aliphatic and Aromatic Ethers."

By Prof. F. M. Jaeger and Jul. Kahn. (Communicated by Prof. P. van Romburgh.)

§ 1. In this communication the results obtained in the measurements of the free surface-energy of a number of ethers, are recorded by us. With respect to the purification-methods and the determination of the specific weights, we can refer to communication II of this series 1); also the arrangement of the data and the significance of the diagrams are completely the same as indicated before. This series includes the following aliphatic terms:

Amylacetate; Diethyl-Oxalate; Diethylmalonate; Diethylbromo-malonate; Diethyl-Ethylbenzylmalonate; Dimethyl and Diaethyltartrates; and the following aromatic substances:

ortho-Nitroanisol; Methyl-, Ethyl-, and Phenyl-Salicylates; Methyl-Cinnamylate.

. I.

	Amylacetate: CH_3 . CO . $O(C_5H_{11})$.						
rature C.	Maximum Pressure H		Surface- tension y	Specific	Molecular Surface-		
Temperature in ° C.	in mm. mer- cury of 0° C.	in Dynes	in Erg. pro	gravity $d_4^{}\circ$	energy # in Erg. pro cm ² .		
-70° -21 0 25.8 46 66.5 86.5 106 125 146	1.099 0.915 0.850 0.771 0.712 0.653 0.600 0.549 0.506 0.461	1465.8 1220.1 1132.6 1028.6 949.4 870.3 799.5 732.9 674.6 614.6	34.6 28.7 26.6 24.1 22.2 20.3 18.6 17.0 15.6 14.2	0.968 0.918 0.896 0.869 0.847 0.827 0.808 0.790 0.774 0.752	907.8 780.0 734.9 679.5 636.8 591.6 550.5 510.8 475.1 440.9		

Molecular weight: 130 11. Radius of the Capillary tube: 0.04803 cm. Depth: $0.1\,$ mm.

The boilingpoint of the carefully dried compound lies at 148.04 C.; at this temperature χ is 14.0 Erg. pro cm².

¹⁾ F. M. JAEGER and M. J. SMIT, These Proc. (1914) p. 365.

	Diethŷl-Oxalate: (C_2H_5) O. CO . CO . CO . $O(C_2H_5)$.						
ature C.	Maximum Pressure H		Surface- tension z	Specific	Molecular Surface-		
Temperature in ° C.	in mm. mer- cury of 0° C	in Dynes	in Erg. pro- cm².	gravity $d_{{f 4}^{\circ}}$	energy // in Erg. pro cm ² .		
26 46 66.7 86.5 106 125 145.5 166 184	1.111 1.025 0.952 0.896 0.818 0.768 0.717	1569.9 1482.5 1366.5 1278 4 1195.1 1091.0 1024.4 955.9 866.6 757.3 637.3	37.0 34.9 32.1 30.0 28.0 25.5 23.9 22.2 20.1 17.6 14.6	1.139 1.110 1.074 1.050 1.025 1.001 0.977 0.954 0.930 0.905 0.883	941.0 903.0 848.8 805.5 764.0 706.8 673.3 635.4 581.1 521.8 440.0		

Molecular weight: 146.08. Radius of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The substance boils at $99.^{\circ}5$ C. constantly, under a pressure of about 12 mm. In solid carbondioxide and alcohol it soon solidifies, and melts at $-41.^{\circ}5$ C. Above 160° C. the ether seems to decompose slowly.

III.

Diethylmalonate: $(C_2H_5) O \cdot CO \cdot CH_2 \cdot CO \cdot O(C_2H_5)$.						
ature			Surface-	Specific	Molecular	
C.	Maximum Pressure H		tension z		Surface-	
Temperature in ° C.	in mm. mer- cury of 0° C.	iń Dynes	in Erg. pro cm ² .	gravity d_{4^0}	energy μ in Erg. pro cm ² .	
-19.9	1.237	1649.2	35.5	1.095	985.3	
0.7	1.167	1555.8	33.5	1.075	941.2	
8.5	1.142	1523.2	32.9	1.068	928.4	
25.2	1.077	1435.9	31.0	1.050	884.8	
34.5	1.044	1391 9	30.0	1.041	861.2	
50.1	0.994	1325.2	28.5	1.025	826.6	
69.2	0.920	1226 8	26.3	1.005	772.9	
102	0.804	1071.8	23.0	0.969	692.5	
124.5	0.723	963.9	20.6	0.945	630.7	
144	0.660	880.2	18.8	0.924	584.3	
148.7	0.649	866.4	18.5	0.919	577.1	
171	0.571	761.6	16.2	0.896	513.9	

Molecular weight: 160.1. Radius of the Capillary tube: 0.04385 cm. Depth: 0.1 mm.

The compound boils constantly at 197.°3 C.; after crystallisation, it melts at -50° C. At 25° C. the specific gravity was 1.0518; at 50° C.: 1 0254. At the boilingpoint the value of χ is: 13.7 Erg pro cm².

IV.

$\textbf{Diethyl-Bromomalonate}: \ (C_2H_5)O \ . \ CO \ . \ CHBr \ . \ CO \ . \ O(C_2H_5).$							
ature C.	Maximum Pressure H		Surface- tension 2	Specific	Molecular Surface-		
Temperature in ° C.	in mm. mer- cury of 0° C.	in Dynes	in Erg. pro	gravity $d_{4^{ m o}}$	energy / in Erg. pro cm².		
-20°.7 0 26 45.5 66.6 86.5 106.5 126 146	1.250 1.165 1.065 0.999 0.943 0.896 0.853 0.815 0.780	1666.5 1553.2 1419.9 1332.5 1257.6 1195.1 1136.8 1086.8 1039.9	39.1 36.4 33.2 31.1 29.3 27.8 26.4 25.3 24.2	1.464 1.436 1.401 1.375 1.347 1.320 1.293 1.266 1.240	1168.2 1101.6 1021.5 968.9 925.4 890.0 856.9 832.8 807.7		

Molecular weight: 239.09. Radius of the Capillary tube: 04803 cm.; Depth: 0.1 mm.

Under reduced pressure (ca. 20 mm.) the substance boils constantly at 121° C.; at -54° C. it becomes a jelly, but does not crystallize. Above 150° C. it begins to be tinged brownish, apparently by beginning deposition. The specific weight at 25° C. is: 1.4022; at 50° C.: 1.3688; at 75° C.: 1.3359; At t° C.: $d_{4^{\circ}}=1.4361-0.001366\ t+0.0000004\ t^2$.

, V.

Diethyl-Ethylbenzylmalonate: $(C_2H_5)O \cdot CO \cdot C(C_2H_5) \cdot (C_7H_7) \cdot CO \cdot O(C_2H_5).$							
Temperature in ° C.	Maximum Pressure H		Surface-	Specific	Molecular Surface-		
	in mm. mer- cùry of 0° C.	in Dynes	in Erg. pro	gravity d_{40}	energy μ in Erg. pro cm ² .		
-20°.2 0 26 45.5 66.6 86.7 106 126 146 166 184 206.5	(2.174) 1.241 1.121 1.050 0.984 0.940 0.901 0.853 0.805 0.759 0.690 0.637	(2898.4) 1654.5 1494.9 1399.9 1311.7 1253.4 1201.2 1136.8 1073.2 1011.9 920.3 849.5	(68.8) 39.0 35.2 32.9 30.8 29.4 28.1 26.6 25.1 23.6 21.4 19.7	1.086 1 072 1.052 1.035 1.016 1.001 0.986 0.971 0.956 0.941 0.927 0.911	(2775.0) 1586.7 1450 1 1370.2 1298 7 1252.1 1208.8 1156.0 1102.2 1047.3 959.2 893.3		

Molecular weight: 278.18. Radius of the Capillar tube: 0.04803 cm. Depth: 0.1 mm.

Under 12 mm. pressure, the substance boils constantly at 189° C.; at -79° C. the liquid becomes a feebly opalescent glass. Already at -20° C. the viscosity is enormous, and at 0° C. again very great. The grow of the gas-bubbles at 0° C. lasted about 40 seconds. The specific gravity at 25° C. is: $d_{4^{\circ}} = 1.0531$; at 50° C.: 1.0322; at 75° C.: 1.0098. At t° C. in general: $d_{4^{\circ}} = 1.0725 - 0.000746 t - 0.0000012 t^{\circ}$.

VI.

	Dimethyltartrate: $(CH_3)O.CO.CH(OH)CH(OH).CO.O(CH_3)$.						
Temperature in ° C.	Maximum Pressure H		Surface- tension	Specific	Molecular Surface-		
	in mm. mer- cury of 0° C.	ın Dynes	in Erg. pro cm².	gravity d_{40}	energy μ in Erg. pro cm ² .		
45° 70.7 90.7 116.2 135.5 *159.6 *190 *210.3	1.490 1.405 1.340 1.255 1.200 1.046 0.974 0.929	1986 6 1873.1 1786.5 1673.2 1599.5 1395.0 1299 2 1238 5	43.2 40.7 38.8 36.3 34.7 32.7 30.4 28.9	1.306 1.281 1.261 1.235 1 216 1 192 1.151 1.131	1144.6 1092.2 1052.2 998.2 964.1 920.7 876.1 842.7		

Molecular weight: 178.08. Radius of the Capillary tube: 0.04439 cm.; in the observations indicated with *, it was: 0.04803 cm. Depth: 0.1 mm.

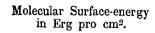
The compound boils under 12 mm. pressure, at 180° C. constantly; at -79° C. it becomes a glass, which crystallizes with extreme slowness; the solid substance melts at $+48^{\circ}$ C. Even at 25° C, the ether is so viscous, that no reliable measurements were possible.

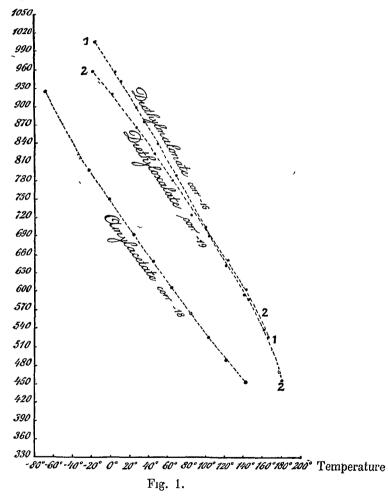
VII.

	$\begin{array}{c} \textbf{Diethyltartrate}:\\ (C_2H_5)O\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot O(C_2H_5). \end{array}$							
Temperature in ° C.	Maximum Pressure H		Surface-	Specific	Molecular Surface-			
	in mm. mer- cury of 0° C.	ın Dynes	in Erg. pro	gravity d_{4^0}	energy μ in Erg. pro cm ² .			
25° 45.3 74.3 91.1 110.1 134.7 150.1 160.3 192.7 212.7		1755.5 1654.4 1512.0 1443.0 1364.9 1263.8 1199.4 1162.7 1019.9 955.9	37.6 35.4 32.3 30.8 29.1 26.9 25.5 24.7 22.0 20.2	1 210 1.191 1.164 1.147 1.129 1.105 1.091 1.081 1.050 1.032	1155.4 1099.3 1018.5 980.8 936.5 878.2 839.6 818.2 743.1 690.2			

Molecular weight: 206.11. Radius of the Capillary tube: 0.04352 cm. Depth: 0.1 mm

Under circa 16 mm. pressure, the boilingpoint is $166^{\circ}.5$ C. At -79° the liquid becomes glassy, and crystallizes very slowly at -20° C.: only after 5 or 6 hours all has got crystalline. The meltingpoint is 15° C. At 0° and lower temperatures the liquid is too viscous, to make reliable measurements possible.





Molecular Surface-energy in Erg pro cm².

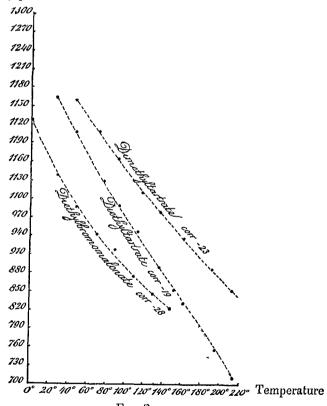


Fig. 2.

400

VIII.

ortho-Nitro-Anisol : (CH_3) O . C_6H_4 . (NO_2) . (2)						
ature C.	Maximum Pressure H		Surface- tension z	Specific	Molecular Surface-	
Temperature in ° C.	in mm. mer- cury of 0° C.	in Dynes	in Erg. pro	gravity d_{4} °	energy μ in- Erg. pro cm ²	
0° 25.4 44.9 70.1 85.3 117 138.2 156 172 191.5 212	1.613 1.537 1.480 1.390 1.340 1.227 1.160 1.109 1.043 0.968 0.850	2150.4 2048.8 1973.8 1853.0 1786.4 1635.8 1546.5 1478.2 1390.8 1290.5 1133.0	50.8 48.4 46.6 43.7 42.1 38.4 36.3 34.7 32.6 30.2 26.5	1.273 1.247 1.227 1.202 1.187 1.156 1.135 1.118 1.102 1.083 1.062	1237.6 1195.4 1165.1 1106.1 1074.6 997.6 947.3 921.8 874.4 819.4 728.8	

Molecular weight: 153.07. Radius of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The substance boils constantly at 272° C.; at - 20° it solidifies, and melts at + 10° C. Above 165° C. a slow decomposition begins. The specific weight at 25° C. is: $d_{4^\circ}=1.2472$; at 50° C.: 1.2218; at 75° C.: 1.1970: at t° generally: $d_{4^\circ}=1.2732-0.001052\,t+0.00000048\,t^2$.

IX.

Methylsalicylate: C_6H_4 (OH). CO . OCH_3 . (1) (2)						
ature C.	Maximum Pressure H		Surface- tension z	Specific	Molecular Surface-	
Temperature in ° C.	in mm. mer- cury of 0° C.	in Dynes	in Erg. pro	gravity d_{4°	energy μ in Erg. pro cm ² .	
-19.8 0.3 * 25 * 45 * 74.7 * 94 114.5 135.2 160.5 192.9 212.2	1.518 1.436 1.372 1.303 1.193 1.124 1.031 0.968 0.867 0.760 0.696	2023.8 1914.8 1829.0 1737.2 1590.1 1498 2 1374 2 1290.5 1155.9 1013.7 928.1	44.2 41.8 39.1 37.1 33.9 31.9 29.8 27.9 24.9 21.8 19.8	1.220 1.202 1.179 1.158 1.128 1.110 1.092 1.073 1.050 1.021 1.003	1102.9 1053.4 998.1 956.4 891.7 848.3 801.2 758.4 686.7 612.6 562.9	

Molecular weight: 152.06. Radius of the Capillary tube: 0.04439 cm.; in the observations, indicated by *, it was 0.04352 cm.
Depth: 0.1 mm.

The substance boils at 217.6 C. constantly; it can be undercooled as far as -50° C, and crystallizes to a solid mass, which melts at -16° C. At the boilingpoint χ is: 19.3 Erg. pro cm². The density at 25° C. is: $d_{4^{\circ}}=1.1787$; at 50° C.: 1.1541; at 75° C.: 1.1285. At t° C.: $d_{4^{\circ}}=1.2023-0.000924$ t-0.0000008 t^{2} .

X.

	Ethylsalicylate: $C_6H_4(OH)$. CO . $O(C_2H_5)$. (2)						
ature C.	Maximum Pressure H		Surface- tension 7	Specific	Molecular Surface-		
Temperature in ° C.	in mm. mer- cury of 0° C.	in Dynes	in Erg. pro cm².	gravity d_{40}	energy μ in Erg. pro cm ² .		
0° * 25 * 45.1 * 74.1 * 94.3 115.1 135.2 159.8 193 212.5	0.963 0.906 0.828 0.723	1794.5 1700.4 1608.5 1479.8 1395.9 1284.1 1207.4 1103.8 964.2 892.1	39.1 36.3 34.3 31.5 29.7 27.8 26.1 23.8 20.7 19.1	1.154 1.130 1.110 1.082 1.063 1.043 1.024 1.001 0.980 0.962	1073.8 1011.0 966.7 903.0 861.6 816.7 776.2 718.6 633.9 592.2		

Molecular weight: 166 08. Radius of the Capillary tube: 0.0 439 cm. in the observations, indicated with * it was: 0.04352 cm.

Depth: 0.1 mm

The substance boils at 231.°2 C. constantly; at -20° C. it solidifies and melts at ca. -10° C. At the boilingpoint χ is 17.6 Erg pro cm². The specific weight at 25° C is:1.1298; at 50° C.:1.1053; at 75° C.:1.0806. At t° it is calculated from: $d_{4^{\circ}} = 1.1541 - 0.000968 \ t - 0.00000016 \ t^{2}$.

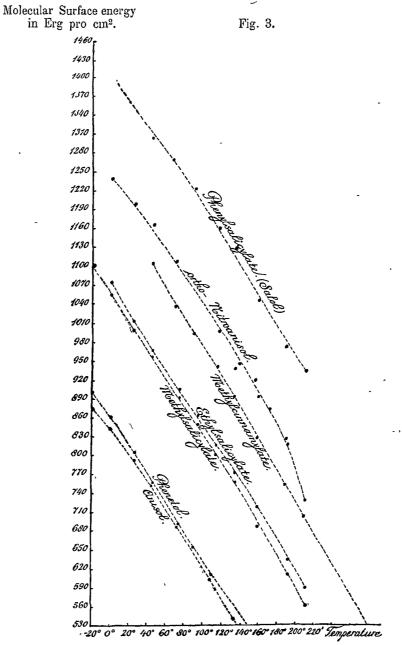
XI.

Phenylsalicylate (Salol): $C_6H_4(OH)$. $CO \cdot O(C_6H_5)$.						
ature C.	Maximum Pressure H		Surface- tension z	Specific	Molecular Surface-	
Temperature in ° C.	in mm. mer- cury of 0° C.	in Dynes	in Erg pro	gravity $d_{4^{\circ}}$	energy μ in Erg. pro cm ² .	
-20°.1 0 25 45 72 90.1 116 135 *160 *189.8 *211.6	(2.613) 1.571 1.485 1.419 1.335 1.272 1.193 1.132 0.971 0.890 0.846	(3482.8) 2095.1 1980.6 1892.3 1779.7 1695.8 1590.4 1509.3 1295.0 1186.7 1128.5	(76.5) 45.7 43.2 41.2 38.7 36.8 34.5 32.7 30.3 27.7 26.3	1.221 1.202 1.179 1.160 1.136 1.120 1.098 1.078 1.055 1.026 1.006	(2396.4) 1446.7 1385.2 1305.1 1272.0 1221.1 1160.0 1130.3 1046.3 974.5 637.5	

Molecular weight: 214.08. Radius of the Capillary tube: 0.04439 cm.; in the observations, indicated with * it was: 0.04803 cm
Depth: 0.1 mm.

Under 12 mm. pressure, the salol boils at 173° C.; at -33° C. it crystallizes spontaneously, and melts at +42° C. It can be undercooled to a very high degree, and possesses a small velocity of crystallisation. At 35° C. the specific gravity is: 1 1697; at 50° C.: 1.1553; at 75° C.: 1.1330

Some other derivatives of aromatic phenoles: Anisol, Phenetol, Anethol, Guajacol, Resorcine-Mono-, and Dimethylethers; Hydrochinon-Dimethylether have been described before by the first of us 1). The temperature-coefficients of these compounds are however also reviewed in the present communication, because they were not mentioned in the one referred to. (Vid. also the preceding communications.)



1) F. M. JAEGER, These Proc., Comm. I. (1914) p. 354 seq.

Methyl-Cinnamylate: C_6H_5 . CH : CH . CO . $O(CH_3)$.							
Temperature in ° C.	Maximum Pressure H		Surface- tension z	Specific	Molecular Surface-		
	in mm. mer- cury of 0° C.	in Dynes	in Erg. pro cm².	gravity $d_{4^{\circ}}$			
45° 71 90.6 116.2 135.4 *159.7 *190.5 *210.9	1.329 1.230 1.166 1.092 1.024 0.868 0.777 0.712	1771.8 1639.8 1554.5 1455.2 1365.2 1157.6 1035.9 949.4	38.7 35.8 33.9 31.7 29.7 27.1 24.2 22.1	1.062 1.038 1.020 0.997 0.980 0.958 0.930 0.911	1105.2 1038.1 994.5 944.2 894.9 829.0 755.1 699.1		

Molecular weight: 162.08. Radius of the Capillary tube: 0.04439 cm.; in the observations, indicated by * it was: 0.04803 cm. Depth: 0.1 mm.

The ether boils at 253.°5 C., and melts at 36.°5 C. At the boiling-point χ is: 18.6 Erg. pro cm². The specific gravity at 35° C. is: $d_{4^{\circ}}=1.0700$; at 50° C.: 1.0573 at 75° C.: 1.0340.

§ 3. Values of the Temperature-coefficients of the molecular surface-energy μ of the studied compounds.

Amylacetate.		Diet	thyl-Oxala	te.
Temperature-interval: $\frac{\partial \mu}{dt}$	in Erg:	Temperature	-interval:	$\frac{\partial \mu}{\partial t}$ in Erg:
between - 70° and - 21°	2,59	between - 20°	and 0°	1,8
-21° and $+66^{\circ}$	2,14	, 0 ₂	and 66°	2,02
66° and 106°	2,03	66°	and 106°	2,2
106° and 148°	1,73	106°	and 146°	2,3
		146°	and 1840	3,6
		Above 146°	a decomp	osition seems
,		slowly to set in	•	
Diethylmalonate.	Diethylbromomalonate.			
between -20° and $+171^{\circ}$	2,52	between — 21°	and 0°	3,20
•		0 2	and 26°	3,08
		26°	and 46°	2,67
	•	46'	and 67°	2,04
		670	and 86°	1,75
		86°	and 106°	1,63
	•	106°	and 126°	1,35
		126°	and 146°	1,23

Diethyl-Ethylbenzylmalo	Dimethyltartrate.			
Temperature-interval: $\frac{\partial \mu}{\partial t}$	in Erg:	Temperature-	interval:	$\frac{\partial \mu}{\partial t}$ in Erg:
. dently cosity. 0° , 26° 26° , 66°	indepen- of the vis- 5,2 3,7	between 45° 117° 160°	" 160°	2,08 1,77
66° "106° 106° "126° 126° "146° 146° "166° 166° "206° Above 166° a slow decomposit to make itself perceptible.	2,25 2,6 2,7 2,75 3,85 cion begins	between 25° 74°		3 2,75
o-Nitroanisol. between 0° and 45° 45° , 172° 172° , 192° 192° , 212° Above 170° a gradual decorates in, which proceeds very services.		between —19	Methylsalid ,°8 and 212	•
Ethylsalıcylate. between 0° and 212°	2,23	Phen between —20	_	te. (Salol). °,6 2,43
Methylcinnamylate. between 45° and 210°,9	2,44	between —21 45 91	Anison o and +4 o , 9	l.
Phenetol. between -12° and 0° 0° , 74°,3 74° , 160° The curve is almost a str with $\frac{\partial \mu}{\partial t}$ = 2,14.	2,0 2,29 2,13 aight line,	between 24°, 75°		,1 2,53
Guajacol. between 26° and 146° 146° " 206°	2,17 2,66	between —20 0 26 46 184	o and 0° o " 26° o " 46° o " 184° o " 206°	cannot be determined independently of the viscosity. 4,3 2,45 1,82 2,97 mposition sets in

Resorcine-Dimethyleth	ier.	Hydrochinon-Dimethylether.		
Temperature-interval: $\frac{\partial \varrho}{\partial t}$	t - ın Erg:	Temperature-interval: $\frac{\partial \mu}{\partial t}$	in Erg:	
between -22° and 0° • 0° , 210°	2,83 2,25	between 66° and 106° 106° " 166° 166° " 206° Up to 166°, this *p-t-curve practically with that of guajo resorcine-dimethylether.		
Pyridine.		√-Picoline.		
between -79° and -20° -20° ", +25° 25° ", 92°	1,79 2,04 1,60	between —70° and — 20°,7 —20°,7 " +126°	2,83 2,02	
Chinoline.				
between -21° and +45°,2 45° , 115° 115° , 230°	1,92 2,10 2,33			

§ 5. Also for these substances one can state, that a decomposition of the compound causes an extraordinarily rapid decrease of the values for χ or μ with increasing temperature: $\frac{\partial \mu}{\partial t}$ becomes much larger in such cases with rising temperature. Furthermore it can be seen from the cases of salol, diethylbenzylmalonate, resorcine-monomethylether, etc., that an extraordinarily great viscosity of the liquid can appreciably diminish the accuracy of the measurements; however the case of dimethyltartrate on the contrary proves, that sometimes reliable results can be obtained, even with very high values of the internal friction.

Groningen, June 1914. Laboratory Inorganic Chemistry of the University.

- Chemistry. "The Temperature-coefficients of the free Surfaceenergy of Liquids, at Temperatures from —80° to 1650° C.: V. Measurements of homologous Aromatic Hydrocarbons and some of their Halogenderivatives". By Prof. Dr. F. M. Jaeger. (Communicated by Prof. P. VAN ROMBURGH.)
- § 1. In order to answer also the question of an eventual dependence between the chemical constitution of liquids and the values of their free surface-energy and of its temperature-coefficient, in 27

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