

Citation:

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Chemistry. — “*The Temperature-coefficients of the free Surface-energy of Liquids, at Temperatures from -80° to 1650° C. III. Measurements of some Aromatic Derivatives.*” By Prof. Dr. F. M. JÄGER and M. J. SMIT. (Communicated by Prof. P. v. ROMBURGH).

§ 1. In continuation of our measurements of organic liquids, the data obtained in the study of a series of aromatic compounds, are reviewed here in tables, quite in the same way as in our former communications¹⁾. This series of substances includes the following terms:

Nitrobenzene; ortho-Nitrotoluene; Aniline; Dimethylaniline; ortho-Toluidine; Thymol; Methyl-, Ethyl-, and Benzyl-Benzoates; Salicylic Aldehyde; Acetophenone, and the non-aromatic compound: α -Campholenic Acid.

With respect to the determination of the specific gravities and the purification of the studied substances, we can refer to the preceding communication; the diagrams also have the same significance, as indicated there.

§ 2. *Aromatic Derivatives.*

I.

Nitrobenzene: $C_6H_5(NO_2)$.					
Temperature in $^{\circ}C$	Maximum Pressure H		Surface- tension γ in Erg. pro cm 2 .	Specific gravity d_{40}	Molecular Surface- energy ν in Erg. pro cm 2 .
	in mm. mer- cury of $0^{\circ}C$	in Dynes			
5 $^{\circ}$	1.538	2050.5	44.4	1.215	964.7
26.6	1.473	1965.8	42.5	1.197	932.7
34.9	1.448	1930.5	41.7	1.190	918.7
55.3	1.371	1827.8	39.5	1.171	879.7
70.8	1.314	1751.8	37.8	1.156	849.0
100	1.198	1596.0	34.4	1.125	786.8
110	1.156	1541.6	33.2	1.115	763.9
126	1.089	1459.8	31.4	1.097	730.4
145.5	1.014	1351.9	29.0	1.075	683.7
172.5	0.903	1204.0	25.8	1.042	621.0

Molecular weight: 123.06. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

The nitrobenzene was carefully dried, several times frozen, and distilled; it boils at $209^{\circ}C$. constantly. At this temperature $\gamma = 21.2$ Erg. pro cm 2 . At $0^{\circ}C$. it solidifies completely. The specific gravity at $25^{\circ}C$. is: $d_{40} = 1.1988$.

¹⁾ F. M. JÄGER and M. J. SMIT, Preceding communication, (1914).

II.

Ortho-Nitrotoluene: $CH_3 \cdot C_6H_4 \cdot (NO_2)$.					
(1) (2)					
Temperature in ° C.	Maximum Pressure H		Surface tension χ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
0.1	1.505	2006.8	43.3	1.177	1032.8
9.6	1.465	1953.1	42.1	1.170	1008.1
* 25	1.416	1887.5	40.9	1.156	987.3
* 34.8	1.375	1833.1	39.7	1.147	963.3
** 49.3	1.257	1675.8	38.2	1.134	934.0
70	1.252	1669.4	35.8	1.115	885.2
101.6	1.132	1509.8	32.4	1.086	815.4
122.6	1.055	1406.5	30.1	1.067	766.5
144	0.971	1295.4	27.7	1.047	714.3
148.6	0.954	1272.4	27.2	1.044	702.8
170	0.864	1151.9	24.5	1.025	640.8

Molecular weight: 137.1. Radius of the Capillary tube: 0.04385 cm.;
in the observations, indicated by *, R was
0.04408 cm.; in these with ** it was:
0.04638 cm.
Depth: 0.1 mm.

The compound boils at 218° C. constantly; the meltingpoint is
-4° C. At the boilingpoint, the value of χ is about 18.1 Erg. pro cm².

III.

Aniline: $C_6H_5(NH_2)$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension χ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mercury of 0° C.	in Dynes			
0°	1.573	2096.5	45.4	1.038	909.3
5.3	1.552	2069.8	44.8	1.032	900.8 ^h
26.2	1.473	1963.8	42.5	1.015	864.0
34.7	1.452	1935.8	41.8	1.008	853.7
54.8	1.371	1827.8	39.5	0.990	816.5
70	1.320	1759.8	38.0	0.976	793.0
100	1.190	1586.5	34.2	0.949	727.2
109.5	1.156	1541.6	33.2	0.941	709.9
126	1.089	1459.8	31.4	0.924	679.6
143	1.027	1369.2	29.4	0.907	644.3
148.8	0.998	1331.8	28.6	0.902	629.0
173.7	0.889	1185.8	25.4	0.877	569.2

Molecular weight: 93.04. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

The liquid boils at 184° C. constantly. It is colourless, and only at
higher temperatures it gets somewhat yellowish. At the boilingpoint,
 χ is: 24.3 Erg. pro cm².

IV.

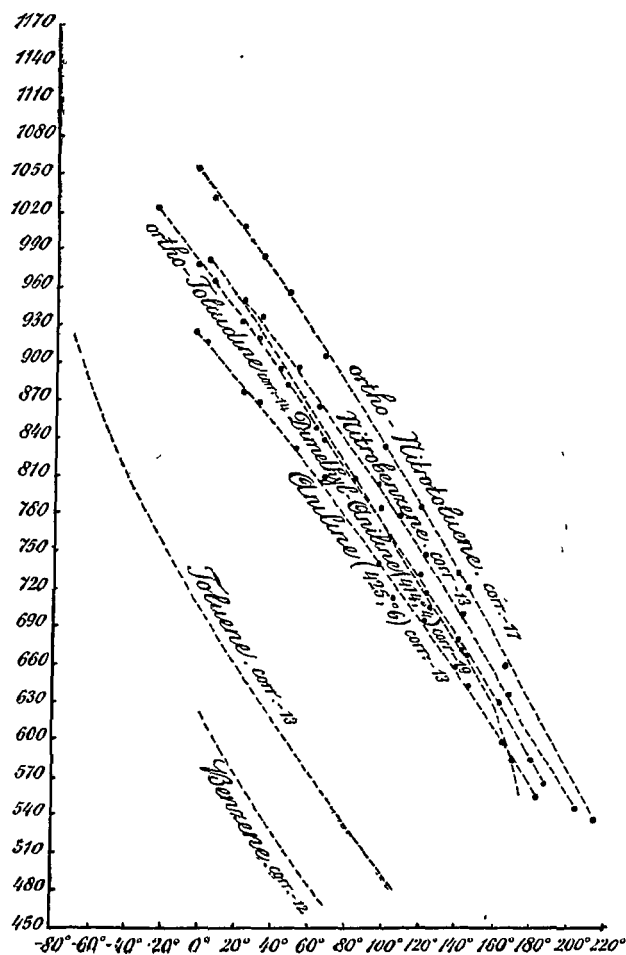
Dimethylaniline; $C_6H_5 \cdot N(CH_3)_2$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension γ in Erg. pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm^2 .
	in mm. mercury of $0^{\circ}C$.	in Dynes			
26 $^{\circ}$	1.165	1553.2	36.6	0.951	926.4
45.5	1.087	1449.1	34.1	0.935	873.0
66.5	1.018	1357.5	31.9	0.917	827.3
86.5	0.959	1278.4	30.0	0.900	787.8
106	0.893	1190.8	27.9	0.884	741.5
125.8	0.831	1107.6	25.9	0.867	697.3
146	0.768	1024.4	23.9	0.850	652.0
166	0.709	945.3	22.0	0.832	608.8
184	0.650	866.1	20.1	0.817	563.0

Molecular weight: 121.11. Radius of the Capillary tube: 0.04803 cm.
Depth: 0.1 mm.

The liquid boils at $191^{\circ}C$. constantly; it solidifies easily and the crystals melt then at $0^{\circ}.5C$. The value of γ at the boilingpoint is about: 19.3 Erg. per cm^2 .

Molecular Surface-energy
in Erg pro cm^2 .

Fig. 1.



V.

Ortho-Toluidine: $CH_3 \cdot C_6H_4 \cdot (NH_2)$ (1) (2)					
Temperature in ° C.	Maximum Pressure H		Surface- tension χ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
-20°	1.573	2098.0	45.4	1.027	1005.8
0.6	1.492	1989.1	43.0	1.013	961.4
9.3	1.465	1953.1	42.2	1.006	947.9
25	1.403	1870.5	40.4	0.992	915.9
34.6	1.375	1833.1	39.6	0.985	902.1
50.1	1.310	1765.8	37.7	0.973	865.8
70.5	1.234	1645.2	35.5	0.957	824.4
101.4	1.133	1510.5	32.5	0.933	767.6
123.2	1.043	1391.0	29.9	0.916	714.9
144	0.957	1277.0	27.4	0.899	663.3
149.5	0.937	1249.8	26.8	0.895	650.8
172	0.831	1108.2	23.7	0.877	583.3

Molecular weight: 107.09. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

The ortho-toluidine boils at 197.4 C. constantly. It is perfectly colourless, but above 180 C. it gets gradually reddish brown. At the boilingpoint $\chi = 19.9$ Erg pro cm².

VI.

Thymol: $(CH_3)_2CH \cdot C_6H_3 \cdot OH(CH_3)$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension χ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
0°	1.176	1567.9	34.2	0.986	975.1
25	1.109	1478.5	32.2	0.968	929.4
45.7	1.054	1405.7	30.6	0.952	893.1
70.7	0.991	1321.9	28.6	0.933	846.0
90.1	0.943	1257.0	27.3	0.920	815.2
115	0.875	1156.6	25.3	0.901	766.0
135.3	0.825	1099.3	23.8	0.887	728.2
* 160	0.703	935.9	21.9	0.867	680.3
* 190.1	0.628	837.0	19.5	0.845	616.2
* 211	0.578	770.3	17.9	0.829	572.9

Molecular weight: 150.11. Radius of the Capillary tube: 0.04439 cm.;
in the determinations indicated by *, R
was: 0.04803 cm.
Depth: 0.1 mm.

The substance melts at 51° C., and boils at 231.°5 C. constantly;
it can be undercooled to a high degree. At the boilingpoint χ is 16.6
Erg. The specific gravity at 24.°4 C. is 0.9639.

VII.

Methylbenzoate: $C_6H_5 \cdot CO \cdot O(CH_3)$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension χ in Erg. pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy ν in Erg. pro cm^2 .
	in mm. mer- cury of $0^{\circ}C$.	in Dynes			
0°	1.405	1873.1	41.0	1.106	1014.1
* 25.1	1.306	1741.2	37.3	1.080	937.4
* 45	1.222	1629.2	34.8	1.059	886.1
* 74.3	1.110	1479.8	31.6	1.028	820.7
* 94.5	1.034	1378.7	29.4	1.006	774.6
115.2	0.946	1261.2	27.4	0.984	732.7
135.3	0.875	1166.9	25.3	0.964	684.8
160	0.791	1054.6	22.8	0.937	629.9
192.5	0.686	914.6	19.7	0.902	558.2

Molecular weight: 136.06. Radius of the Capillary tube: 0.04439 cm.; in the observations indicated by *, the radius was: 0.04352 cm.
Depth: 0.1 mm.

The boilingpoint of the compound lies at 195. $^{\circ}2$ C. The liquid can be undercooled as far as -21° C.; then it crystallizes, and the crystals melt at about -15° C. At the boilingpoint the value of χ is: 19.4 Erg. pro cm^2 .

VIII.

Ethylbenzoate: $C_6H_5 \cdot CO \cdot O(C_2H_5)$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension χ in Erg. per cm^2 .	Specific gravity d_{40}	Molecular Surface- energy ν in Erg. pro cm^2 .
	in mm. mer- cury of $0^{\circ}C$.	in Dynes			
$-20^{\circ}5$	1.338	1783.8	39.0	1.081	1045.7
0	1.271	1694.1	37.0	1.066	1001.3
* 25	1.213	1617.6	34.6	1.047	947.7
* 45.1	1.148	1530.4	32.7	1.032	904.3
* 75	1.044	1392.4	29.7	1.009	833.8
* 94.4	0.972	1295.9	27.6	0.995	782.1
114.6	0.892	1189.4	25.8	0.980	738.5
135.4	0.833	1110.6	24.0	0.964	694.6
160.2	0.740	986.7	21.3	0.945	624.7
192.1	0.649	865.0	18.6	0.921	554.9
200	0.628	838.0	18.0	0.914	539.7

Molecular weight: 150.08. Radius of the Capillary tube: 0.04439 cm.; in the observations indicated by * this radius was: 0.04352 cm.

The compound boils at 210. $^{\circ}8$ C. It can be undercooled as far as -79° C., and then slowly crystallizes to a white mass, which melts at -57° C. At the boilingpoint, χ is 17.4 Erg. pro cm^2 . The great viscosity of the liquid at -70° C. makes accurate measurements impossible.

IX.

Benzylbenzoate: $C_6H_5 \cdot CO \cdot O(CH_2 \cdot C_6H_5)$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension γ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
-21.8°	1.622	2162.4	47.4	1.153	1533.2
0	1.548	2063.5	45.2	1.136	1476.6
25	1.456	1941.9	42.5	1.115	1405.7
45	1.384	1851.8	40.5	1.099	1352.5
70.8	1.294	1725.8	37.6	1.078	1271.9
90.8	1.230	1640.0	35.8	1.062	1223.2
106.2	1.179	1572.4	34.3	1.042	1186.9
135.1	1.092	1455.2	31.7	1.027	1107.6
*159.9	0.949	1265.9	29.8	1.006	1055.6
*190	0.890	1186.7	27.9	0.982	1004.4
*211.5	0.849	1132.6	26.6	0.965	968.8

Molecular weight: 212.10. Radius of the Capillary tube: 0.04439 cm.; in the observations indicated by *, this radius was: 0.04803 cm.
Depth: 0.1 mm.

The substance boils constantly at 308° C.; it can be undercooled as far as -70° C., and then crystallizes. The meltingpoint is somewhat higher than +12° C. At the boilingpoint γ is 22.6 Erg pro cm². The density at 25° C. is: $d_{40} = 1.1151$; at 50° C.: 1.0940; at 75° C.: 1.0724; at t° C.: $d_{40} = 1.1357 - 0.000814 t$.

X.

Salicylic Aldehyde: $C_6H_5 \cdot COH$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension γ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
0°	1.534	2045.5	44.8	1.176	989.4
25	1.443	1923.8	42.1	1.152	942.6
45.5	1.368	1823.8	39.9	1.132	903.9
70.7	1.274	1698.6	37.1	1.108	852.5
90.5	1.205	1606.5	35.0	1.090	813.1
116.2	1.115	1486.8	32.4	1.066	764.0
135.4	1.053	1403.8	30.6	1.052	727.9
*160	0.896	1195.1	28.1	1.030	677.9
*190	0.796	1061.9	24.9	1.002	607.2

Molecular weight: 122.05. Radius of the Capillary tube: 0.04439 cm.; in the with * indicated observations, this radius was: 0.04803 cm. Depth: 0.1 mm.

The boilingpoint is constant at 192.°5 C.; the substance soon solidifies, and melts at -7° C. At 25° C. the specific gravity is: $d_{40} = 1.1525$; at 50 C.: 1.1282; at 75° C.: 1.1036. At t° in general: $d_{40} = 1.1765 - 0.000954 t - 0.00000024 t^2$. At the boilingpoint, the value of γ is: 25.4 Erg. pro cm².

XI.

Acetophenone: $CH_3 \cdot CO \cdot C_6H_5$.					
Temperature in $^{\circ}C$	Maximum Pressure H		Surface- tension γ in Erg. pro cm 2 .	Specific gravity d_{40}	M en Erg
	in mm. mer- cury of $0^{\circ}C$.	in Dynes			
24.8	1.375	1833.6	40.1	1.024	
44.7	1.277	1703.1	37.2	1.007	
71	1.169	1558.9	34.0	0.984	
90.3	1.098	1464.2	31.9	0.967	
117	1.017	1356.2	29.5	0.945	
135.3	0.966	1288.6	28.0	0.929	
*160	0.824	1099.3	25.8	0.907	
*189.9	0.750	999.4	23.4	0.881	
*200	0.728	970.2	22.7	0.872	

Molecular weight: 120.06. Radius of the Capillary tube: 0.04 cm. in the observations indicated by radius was: 0.04803 cm.
Depth: 0.1 mm.
The compound boils constantly at 201.5 C.; and becomes $-20^{\circ}C$; it melts at $+20^{\circ}C$. At the boilingpoint the value 22.6 Erg. pro cm 2 . The specific gravity at $25^{\circ}C$. is: $d_{40} = 1.0026$.
 $50^{\circ}C$.: 1.0026.

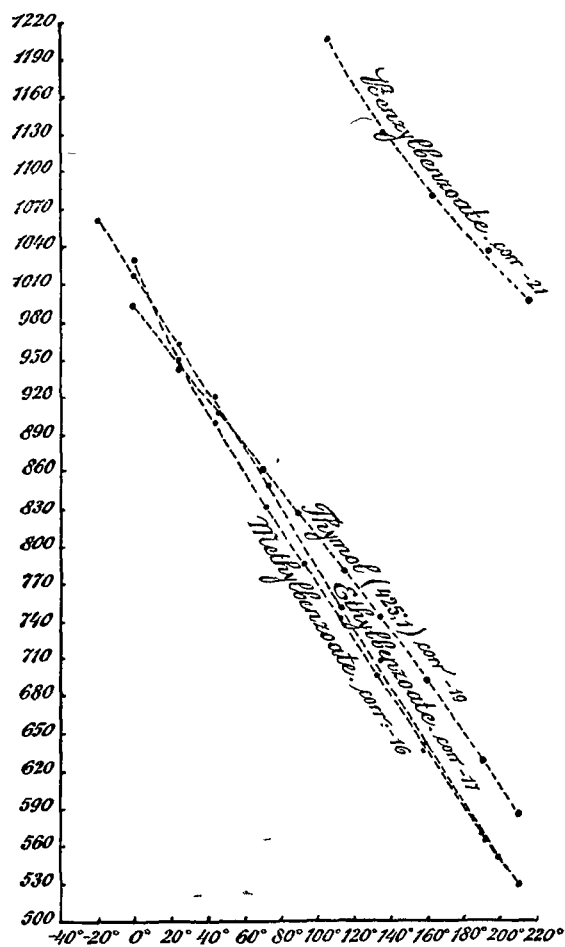
XII.

α -Campholenic Acid: $(CH_2)_2 \cdot C \cdot CH \cdot CH_2 \cdot CO \cdot OH$. $(CH_3) \cdot C \cdot CH$					
Temperature in $^{\circ}C$	Maximum Pressure H		Surface- tension γ in Erg. pro cm 2 .	Specific gravity d_4	M en Erg
	in mm. mer- cury of $0^{\circ}C$.	in Dynes			
-19.8	(1.695)	(2259.8)	(53.6)	1.030	(
0	1.177	1569.2	37.0	1.016	
25	1.077	1436.6	33.8	0.999	
45.4	1.019	1358.5	31.9	0.985	
70	0.953	1270.5	29.8	0.969	
85.3	0.915	1220.1	28.6	0.960	
117	0.846	1128.5	26.4	0.939	
138.1	0.805	1073.2	25.1	0.925	
156	0.771	1027.9	24.0	0.913	
172	0.728	970.2	22.6	0.902	
191.7	0.664	885.2	20.6	0.889	
212	0.608	810.6	18.8	0.876	

Molecular weight: 168.13. Radius of the Capillary tube: 0.04 cm. Depth: 0.1 mm.
Under a pressure of 12 mm., the compound boils constantly at $153^{\circ}C$. Below $0^{\circ}C$. the liquid is extremely viscous; although growing of the gas-bubbles lasted about 50 seconds, the measurement at $-19^{\circ}C$. cannot be considered to be very reliable. The substance solidifies at $-79^{\circ}C$; above $160^{\circ}C$. it gets yellow by a slow pyrolytic decomposition.

Molecular Surface-energy
in Erg pro cm².

Fig. 2.



§ 3. Values of the Temperature-coefficients of the molecular Surface-energy μ .

<i>Nitrobenzene.</i>		<i>o-Nitrotoluene.</i>	
<i>Temperature-interval:</i>	$\frac{\partial \mu}{\partial t}$ in Erg:	<i>Temperature-interval:</i>	$\frac{\partial \mu}{\partial t}$ in Erg:
between 5° and 35°	1,53	between 0° and 25°	1,81
35° " 71°	1,93	25° " 49°	2,19
71° " 110°	2,16	49° " 123°	2,29
110° " 145°	2,25	123° " 144°	2,42
145° " 173°	2,31	144° " 170°	2,82
<i>Aniline.</i>		<i>Dimethylaniline.</i>	
between 0° and 35°	1,57	between 26° and 46°	2,72
35° " 70°	1,73	46° " 184°	2,23
70° " 174°	2,16		
<i>o-Toluidine.</i>		<i>Thymol.</i>	
between -20° and +101°	1,98	between 0° and 160°	1,83
101° " 144°	2,44	160° " 211°	2,09
144° " 172°	2,85		
Above 160° a gradual decomposition with colouring of the liquid, sets in.			
<i>Methylbenzoate.</i>		<i>Ethylbenzoate.</i>	
between 0° and 25°	3,0	between -20° and +200°	2,29
25° " 45°	2,6		
45° " 192°	2,21		
<i>Benzylbenzoate.</i>		<i>Salicylic Aldehyde.</i>	
between -22° and +135°	2,70	between 0° and 160°	1,98
135° " 160°	2,08	160° " 190°	2,19
160° " 211°	1,66		
<i>Acetophenone.</i>		<i>α-Campholenic Acid.</i>	
between 25° and 45°	2,99	between -19°,8 and 0°	cannot be determined independently of the viscosity
45° " 71°	2,45	0° " 25°	3,39
71° " 90°	2,19	25° " 45°	2,42
90° " 160°	1,76	45° " 85°	2,12
160° " 200°	1,61	85° " 117°	1,76
		117° " 138°	1,59
		Above 138° (decomposition) ca. 2,6	

Besides some straight lines, there are found here several curves for the dependence of μ and t , showing in contradistinction with the formerly described ones, the shape of that of *water*.

Groningen, June 1914.

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