Resorcine-Dimethylether.

Temperature-interval:	$\frac{\partial \mu}{\partial t}$ *in Erg:*
between —22° and 0°	2,83
0° „ 210°	2,25

Pyridine.

between —79° and —20°	1,79
—20° „ +25°	2,04
25° „ 92°	1,60

Chinoline.

between —21° and +45°,2	1,92
45° „ 115°	2,10
115° „ 230°	2,33

Hydrochinon-Dimethylether.

Temperature-interval:	$\frac{\partial \mu}{\partial t}$ *in Erg:*
between 66° and 106°	2,11
106° „ 166°	2,46
166° „ 206°	2,88

Up to 166°, this μ-t-curve coincides practically with that of *guajacol* and of *resorcine-dimethylether.*

γ-Picoline.

between —70° and — 20°,7	2,83
—20°,7 „ +126°	2,02

§ **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 Surface-energy 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

this communication the results of the measurements are recorded, made with a series of homologous hydrocarbons and some of their halogen-derivatives. With respect to the methods of purification, the determination of the specific gravities, and the significance of the diagrams, we can refer to the previous communications.

This series includes the following terms:

Benzene; *Toluene*; *para-Xylene*; *Mesitylene*; *Pseudocumene*; *Triphenylmethane*; *Chlorobenzene*; *Bromobenzene*; *meta-Dichlorobenzene*; *para-Fluorobromobenzene*; *meta-Fluorotoluene*; and *para-Chlorotoluene*.

For the purpose of comparison with benzene, also *Cyclohexane* was taken into account here; the data relating to benzene were already published in a former paper [1]), but are repeated here once more for comparison with the other hydrocarbons. The obtained results are put together in tables, in the ordinary way.

§ 2. *Aromatic Hydrocarbons and some Halogenderivatives.*

I.

Cyclohexane: C_6H_{12}.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity d_{4°	Molecular Surface-energy γ in Erg. pro cm².
9°	0.830	1106.8	28.3	0.788	636.7
19	0.785	1046.5	26.7	0.778	605.9
24.6	0.755	1007.6	25.7	0.773	585.7
40	0.682	909.2	23.1	0.768	529.2
58	0.601	801.2	20.3	0.744	474.6
70	0.548	730.6	18.4	0.732	434.9
80	0.504	671.6	16.9	0.723	402.7

Molecular weight: **84.1.** Radius of the Capillary tube: 0.05240 cm. Depth: 0.1 mm.

The liquid boils constantly at 80.°7 C.; at this temperature the value of χ is: **16.7** Erg. pro cm². It solidifies at 10 C.; the crystals melt at +8° C. The specific gravity at 25° C. is. 0.7733; at 35° C.: 0.7645; at 50° C.: 0.7515. At $t°$ C.: $d_{4^\circ} = 0.7958 - 0.000913\,t + 0.00000053\,t^2$.

[1]) F. M. JAEGER and M. J. SMIT; F. M. JAEGER and J. KAHN; F. M. JAEGER, these Proc., Comm. I, II, IV. (1914).

II.

Benzene: C_6H_6.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
5.4°	1.077	1436.7	30.9	0.895	607.7
9.5	1.055	1406.5	30.2	0.889	596.6
25.1	0.969	1291.9	27 7	0.873	553.8
35	0.920	1226.5	26.3	0.862	530.3
55	0.836	1114 6	23.8	0.841	487.8
74.6	0.757	1009.2	21.6	0.817	451.4

Molecular weight: **78.05.** Radius of the Capillary tube: 0.04385 cm. Depth: 0.1 mm.

The compound was already formerly described [1]), and is here only mentioned for purpose of comparison. The boilingpoint is 80.°5 C.; at this temperature χ is: **20.7** Erg. pro cm².

[1]) JAEGER, These Proceedings, Comm. I. (1914).

III.

Toluene: $CH_3 . C_6H_5$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
—71°	1.385	1846.5	43.7	0.956	918.1
—21	1.090	1453.2	34.3	0.905	747.6
0	1.006	1340.8	31.6	0.884	699.5
26	0.906	1207.6	28.4	0.860	640.3
46	0.831	1107.6	26.0	0.841	595.0
66.6	0.756	1007.7	23.6	0.823	547.9
86.5	0.693	924.4	21.6	0.803	509.7
106	0.637	849.5	19.8	0.783	475.2

Molecular weight: **92.06.** Radius of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The commercial toluene appeared always to manifest a turbidity of the liquid at —22° and —79° C.; a solid substance in little quantities separated at the walls of the tube. The here used toluene therefore was especially prepared by distillation of sodium phenylacetate; it was dried by means of phosphorpentoxide, and boils at 109.°4 C. Down to —20° C. it remains perfectly clear; at - 79° C. it shows, as e.g other hydrocarbons (pseudocumene) do, a slight turbidity. At the boilingpoint χ is **19.5** Erg. pro cm².

IV.

para-Xylene: $(CH_3)_{(1)} . C_6H_4 . (CH_3)_{(4)}$.

Temperature in ° C.	Maximum Pressure H		Surface-tension λ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
25°7	0.928	1236.7	29.1	0.857	723 3
45.9	0.853	1137.2	26.7	0.839	672.6
66	0.774	1031.9	24.2	0.821	618.5
86.5	0.709	945.2	22 1	0.802	573.7
106	0.648	863.9	20.1	0.784	529.8
126	0.597	794.6	18.5	0.766	495.2

Molecular weight: **106 08.** Radius of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The substance boils at 136.°2 C. and melts at 15° C. At the boiling-point γ is about **18 1** Erg. pro cm². At 20° the density is $d_{4°} = 0.8611$.

V.

Mesitylene: $(CH_3)_3 . C_6H_3 .$ **(1-3-5-).**

Temperature in ° C.	Maximum Pressure H		Surface-tension λ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—20°.8	1.141	1521.1	32.6	0.897	853.2
0	1.061	1415.4	30.3	0.880	803.2
25.5	0.972	1296.0	27.7	0.859	746.2
45.2	0.907	1208.7	25.8	0.843	703.8
74.7	0.807	1075.4	22.9	0.818	637.3
91.3	0 755	1006.4	21.4	0.804	602.5
110	0.700	933.0	19.8	0.788	565.0
134.5	0.631	841.0	17.8	0.768	516.7
150.5	0.585	781 2	16.5	0.754	484.8
160.5	0.562	749.3	15.8	0.741	469 7

Molecular weight: **120.1.** Radius of the Capillary tube: 0.04352 cm. Depth: 0 1 mm.

The compound boils at 162.°8 C. constantly. At —46° C it solidifies to an aggregate of long, silky needles.

VI

Pseudocumene: $(CH_3)_3 . C_6H_3$ **(1-2-4-).**

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg. pro cm².	Specific gravity d_4	Molecular Surface-energy ν in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—21°	1.084	1444.9	34.1	0.910	883.9
0	1.031	1374.1	32 4	0.893	850.5
26	0.953	1270.1	29 9	0 871	798.0
46	0.890	1186.4	27.9	0 855	753.9
66 5	0.828	1103.5	25.9	0.839	708.8
86.5	0.768	1024.4	24.0	0.823	665.2
105	0.725	966.1	22.6	0.807	634.7
125	0 656	874 5	20.4	0.792	580.1
145 9	0.600	799.5	18.6	0.776	536.2
166	0.525	699.6	16.2	0.760	473.5

Molecular weight: **120.1.** Radius of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The substance boils at 168.°5 C. constantly. It solidifies at —79° C.; the meltingpoint is about —60° C. At the boilingpoint the value of χ is **15.8** Erg. pro cm².

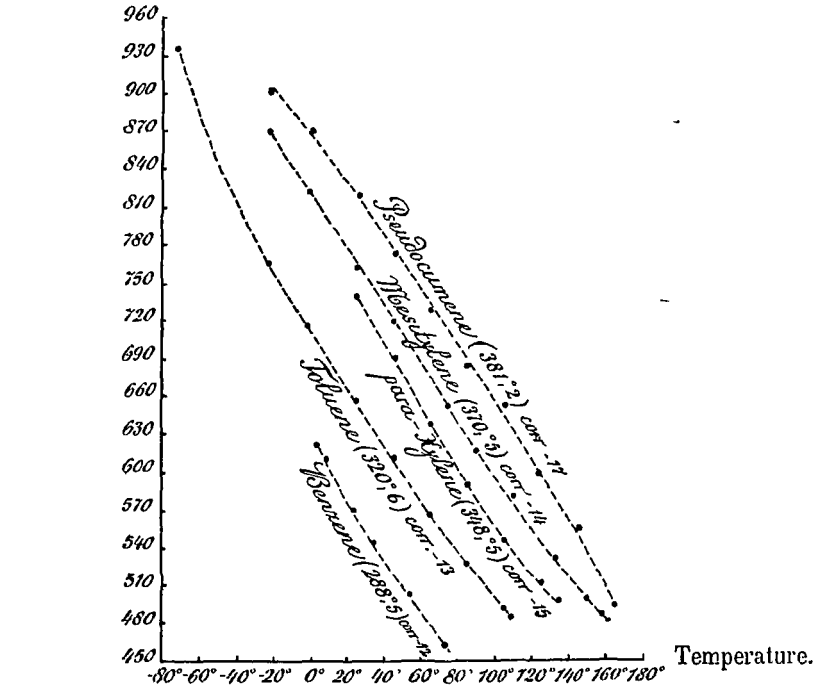


Fig. 1.

VII.

Triphenylmethane: $CH(C_6H_5)_3$.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
138.4°	1.074	1432.4	33.7	0.984	1330.5
156	1.044	1391.9	32.8	0.971	1302.6
171	0.999	1332.5	31.3	0.959	1257.1
194	0.909	1211.9	28.4	0.942	1154.4
212	0.833	1110.5	26.0	0.928	1067.4

Molecular weight: **244.11.** Radium of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The meltingpoint of the compound is 92° C.; it is hardly possible to keep it in undercooled condition. Above 165° C. a slow decomposition begins; finally the liquid is coloured brown. The specific gravity $d_{4°}$ is at 95° C.: 1,017; at 100°: 1,013; at 125° C.: 0,994; at 150° C.: 0,975; it was determined by means of the hydrostatic balance. At $t°$ $d_{4°} = 1{,}013 - 0{,}00076\ (t - 100)$.

VIII.

Chlorobenzene: C_6H_5Cl.

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension χ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
—16°	1.252	1668.8	38.0	1.144	809.6
0	1.184	1578.3	35.9	1.128	772.1
**25	1.143	1524.5	32.9	1.101	719.1
**35	1.099	1465.5	31.6	1.090	695.3
50	0.980	1306.6	29.6	1.073	658.1
70.5	0.893	1190.2	26.9	1.051	606.4
90	0.805	1079.0	24.2	1.029	553.3
*102	0.807	1075.4	22.7	1.016	523.4
*114.5	0.751	1001.8	21.1	1.003	490.7
*122	0.717	955.9	20.1	0.995	470.0

Molecular weight: **112.50.** Radius of the Capillary tube: 0.04638 cm.; with the observations, indicated by *, R was 0.04352 cm.; with those: **, it was: 0.04408 cm.
Depth: 0.1 mm.

The compound boils at 131° C. constantly; at —34.°5 C. it is completely crystallized.

IX.

Bromobenzene: C_6H_5Br.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—17.5°	1.394	1858.6	42.2	1.546	918.4
2.1	1.309	1746.4	39.6	1.519	872.0
*25	1.267	1698.5	36.5	1.488	814.9
*35.6	1.229	1638.5	35.2	1.474	790.8
*49.8	1.172	1562.5	33.5	1.456	758.8
71.5	1 032	1375.6	31.0	1.425	712.3
90.5	0.953	1270.5	28.5	1.399	663.0
** 125.5	0.875	1167.3	24.5	1.351	583.3
** 153	0.758	1011.0	21.1	1.313	512.0

Molecular weight: **156.96.** Radius of the Capillary tube: 0 04638 cm.; in the observations, indicated by * R was: 0.04408; in those by **, it was: 0.04352 cm. Depth: 0.1 mm.

The compound boils constantly at 154° C.

X.

meta-Dichlorobenzene: $C_6H_4Cl_2$ **(1-3-).**

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
	in mm. mercury of 0° C.	in Dynes			
—22°	1.433	1910.3	41.6	1.332	956.8
0	1.328	1770.6	38.5	1.309	895.9
25	1.230	1640.0	35.6	1 282	840.0
44.9	1.156	1540.9	33.4	1.260	797.9
71	1.061	1414.7	30.6	1.230	742.2
90.7	0.993	1324 6	28.6	1.213	700.2
116.4	0.912	1216.5	26.2	1.185	651.5
136	0.858	1144.4	24.6	1.164	619.0
*160	0.737	982.7	22.8	1.138	582.4

Molecular weight: **146.93.** Radius of the Capillary tube: 0.04439 cm.; in the observation, indicated with *, the radius was: 0.04803 cm. Depth: 0.1 mm.

The boilingpoint is at 172.°5 C. constant; the liquid can be undercooled to a high degree, but once solidified, it melts at —19° C. At the boilingpoint χ is: **22.2** Erg pro cm². The specific gravity at 25° C. is: 1.2824; at 50° C.: 1.2543; at 75° C.: 1.2253; at t° C.: $1.3096-0.00107\,t-0.00000072\,t^2$.

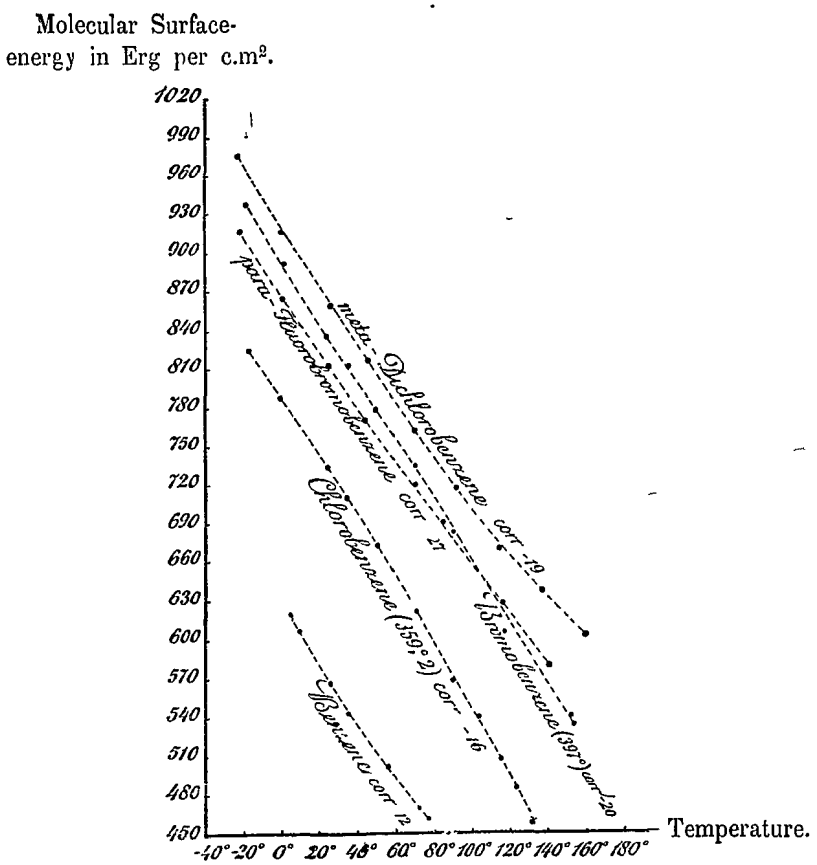


Fig. 2.

XI.

para-Fluorobromobenzene: $C_6H_4 . F . Br$ (1-4-).

Temperature in ° C.	Maximum Pressure H		Surface-tension $\varkappa$ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
	in mm. mercury of 0° C.	in Dynes			
—21°	1.281	1707.8	39.8	1.654	890.2
0	1.198	1597.2	37.2	1 626	841.5
25.5	1.106	1474.1	34.3	1.590	787.6
45.3	1.031	1374.1	31.9	1 561	741.6
70	0.953	1270.1	29 4	1.522	695 1
84.7	0.906	1207.6	27.9	1.504	663.8
117	0.810	1079 9	24.8	1 460	602.8
138	0.734	978.6	22.4	1.436	550.5

Molecular weight: **174.95.** Radius of the Capillary tube: 0.04803 cm. Depth 0.1 mm.

The boilingpoint is constant at 150° C.; the value of $\varkappa$ there is: **21.2** Erg. pro cm². The specific gravity at 25° C. is: $d_{4°} = 1.5908$; at 50 C.: 1.5538; at 75° C.: 1.5147. At $t°$ it is: $d_{4°} = 1.6257 - 0.00135\ t - 0.00000168\ t^2$.

XII.

meta-Fluorotoluene: $CH_3 . C_6H_4 . F$ (1) (3)

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension γ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg. pro cm².
—71°	1.337	1782.5	42 1	1.097	909.0
—20.5	1.090	1453.3	34.2	1.041	764 7
0	1.006	1340.9	31 5	1.021	713 5
25.4	0.906	1207.9	28.3	0.994	652 6
45.3	0.839	1118.5	26.2	0.973	612 8
70.2	0.760	1021.2	23.8	0.947	566.8
84.9	0.721	961.9	22.4	0.932	539.2

Molecular weight: **110.06.** Radius of the Capillary tube: 0.04803 cm. Depth· 0.1 mm.

The boilingpoint of the substance is 114°.5 C.; γ is there: **20.2** Erg. pro cm². The density at 25° C. is: $d_{4°} = 0.9942$; at 50° C. 0.9680; at 75° C.: 0.9420. At $t°$ it is calculated from: $d_{4°} = 1.0206 - 0.00106\,t + 0.00000016\,t^2$.

XIII.

para-Chlorotoluene: $CH_3 . C_6H_4 Cl$ (1) (4)

Temperature in ° C.	Maximum Pressure H in mm. mercury of 0° C.	Maximum Pressure H in Dynes	Surface-tension γ in Erg. pro cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg pro cm².
25°	1.137	1515.8	32.9	1.065	795.0
44.7	1.059	1410.2	30 6	1.045	748.8
71	0.959	1279.6	27.7	1.018	689.8
90.2	0.895	1193.2	25.8	0.999	650.6
116.1	0.813	1083.9	23.4	0.973	600.6
135.7	0.760	1013 8	21 8	0.953	567.3
*160	0.653	870.3	20.2	0.928	535.1

Molecular weight: **126.51.** Radius of the Capillary tube: 0.04439 cm.; in the observation, indicated by *, it was: 0 04803 c.m. Depth: 0.1 mm.

The substance boils constantly at 162.°5 C., it solidifies at —22° C., and melts at +7 °5 C. At the boilingpoint γ is **20.1** Erg. pro cm².

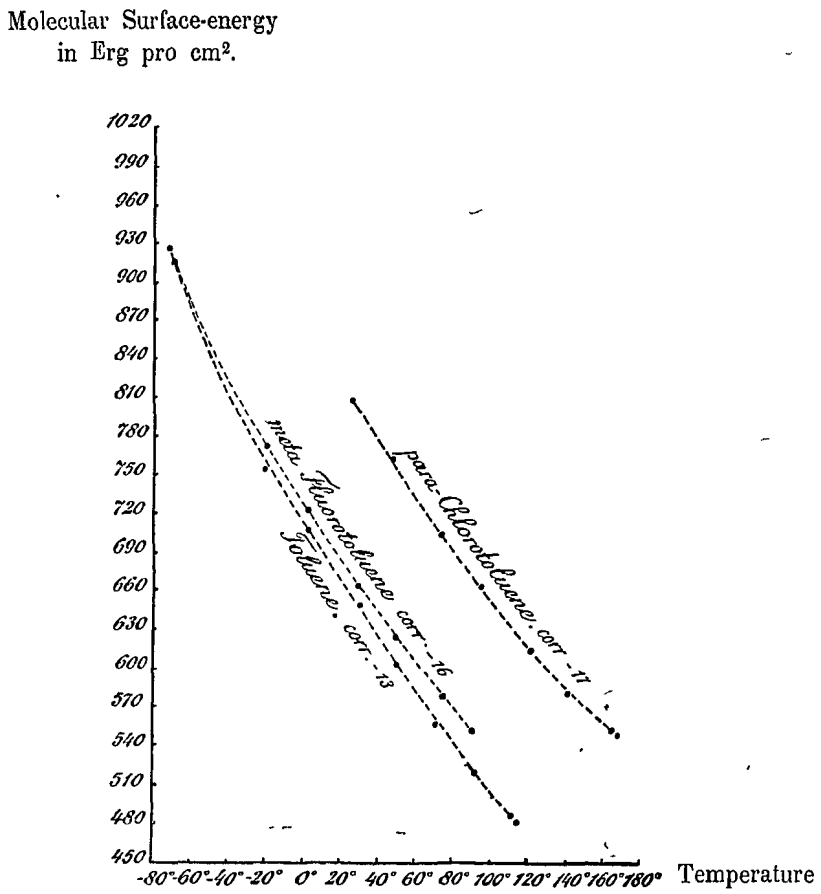


Fig. 3.

§ **3**. *Values of the Temperature-coefficients of the molecular Surface-energie* μ *of the liquids here studied.*

Cyclohexane.					
Temperature-interval:				$\frac{\partial \mu}{\partial t}$ *in Erg:*	
between	9°	and	80°	3,32	
This value is remarkably great; the curve is almost a straight line however.					
Toluene.					
between	−71°	and	−21°	3,40	
	−21	„	66,6	2,27	
	67	„	86,5	1,90	
	86,5	„	109	1,76	

Benzene.					
Temperature-interval:				$\frac{\partial \mu}{\partial t}$ *in Erg:*	
between	5°,4	and	25°,1	2,73	
	25	„	55	2,20	
	55	„	74,6	1,85	
para-Xylene.					
between	25°,5	and	45°	2,53	
	45	„	86	2,43	
	86	„	106	2,21	
	106	„	126	1,71	

Mesitylene.

Temperature-interval:			$\frac{\partial \mu}{\partial t}$ *in Erg:*
between	−20°,8	and 0°	2,40
	0	„ 75	2,20
	75	„ 110	2,06
	110	„ 150	1,97

Triphenylmethane.

between	138°,4	and 156°	1.59
	156	„ 171	3.03
	171	„ 194	4.46
	194	„ 212	4.83

Bromobenzene.

between	−17,°5	and +125,°5	2,38
	125,5	„ 153	2,53

para-Fluorobromobenzene.

between	−21°	and 0°	2,41
	0	„ 45	2,09
	45	„ 117	1.97
	117	„ 150	2,49

para-Chlorotoluene.

between	25°	and 45°	2,33
	45	„ 71	2,23
	71	„ 116	1,97
	116	„ 160	1,49

Pseudocumene.

Temperature-interval:			$\frac{\partial \mu}{\partial t}$ *in Erg:*
between	−21°	and 0°	1,60
	0	„ 26	2,00
	26	„ 146	2,18
	146	„ 166	3,0

Chlorobenzene.

between	−16°	and +25°	2,20
	25	„ 50	2,42
	50	„ 122	2,60

meta-Dichlorobenzene.

between	−22°	and 0°	2,79
	0	„ 25	2,23
	25	„ 91	2,11
	91	„ 117	1,88
	117	„ 136	1,64
	136	„ 160	1,51

meta-Fluorotoluene.

between	−71°	and −20°,5	2,85
	−20,5	„ 0	2,49
	0	„ 25,4	2,38
	25,4	„ 45,3	1,99
	45,3	„ 84,9	1,85

Especially the last mentioned four cases prove once more very strikingly the fact, that $\frac{\partial \mu}{\partial t}$ cannot be considered as a constant, but that it is itself a function of temperature: in most cases in such a way, that it will decrease with increasing temperature. With *chloro-* and *bromobenzene* however evidently just the reverse happens. In the same way *benzene, toluene, p-xylene* and *mesitylene* belong to the first group of substances, while the isomeric *pseudocumene* manifests on the contrary an increase of $\frac{\partial \mu}{\partial t}$ with rising temperature. The deviations of the linear decline are so great and in most cases so systematical, that they can by no means be accounted for by experimental errors; the variability of $\frac{\partial \mu}{\partial t}$ with the temperature must therefore be considered as an essential fact.

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

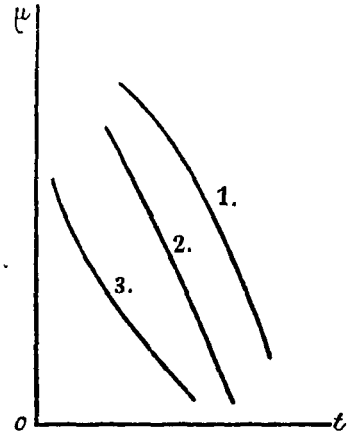
Chemistry. — "*The Temperature-coëfficients of the free Surface-energy of Liquids, at Temperatures from* — 80° *to* 1650°*C: VI. General Remarks*". By Prof. Dr. F. M. JAEGER. (Communicated by Prof P. ROMBURGH).

§ 1. If we wish to use the results up to now obtained in the study of these more than seventy organic and about ten inorganic liquids, to draw some more general conclusions, the following remarks in this respect may find a place here.

In the first place it is proved once more, that *the free surface-energy of liquids*, — also in the peculiar case of the *electrolytically conducting*, molten salts studied at very high temperatures, — *always decreases with increasing temperature*. This fact, an exception to which also within the temperature-interval hitherto investigated has never been stated, must be esteemed in every respect quite in concordance with the views about the origin of such surface-tensions. It is immediately connected with the other fact, that a *decrease* of the molecular surface-layer must be accompanied by a heat-*evolution*, an *increase* of that layer however with a heat-*absorption*, if the temperature is to remain constant. Furthermore this gradual diminution of χ with increasing temperature is in full agreement with the continual levelling of the differences in properties between the liquid phase and its coexistent vapour, when the temperature is gradually rising: at the critical temperature the value of χ must have become zero [1]).

Of more importance for our purposes however are the following results:

I. A *linear* dependence of χ and t appears in general *not* to exist. The observations prove the possibility of all the three imaginable principal species of χ-t-curves: the type 1, with a concave shape towards the temperature-axis; the type 3 with a shape convex to that axis, and the *rectilinear* type 2. Besides there are found some rare cases of combinations of these three principal types. Characteristic for type N°. 1 is, that $\frac{d\chi}{dt}$ will *increase* with rising temperature, while it *decreases* under those circumstances on the curves of type 3;



[1]) The critical temperatures of the studied liquids, are as far as known, in the diagrams indicated between ( ), behind the names of the different substances.