

Citation:

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§ 20. In the case of POTASSIUMCHLORATE: $KClO_3$, the maximum pressure H was 3,573 mm. mercury at $413^{\circ}.5$ C; at $443^{\circ}.5$ C. it was: 3,540 mm. The radius of the here used silver-capillary tube being: = 0.03460 cm., the free surface-energy is calculated:

At $413^{\circ}.5$ C. $\chi = 82,4$ Erg. pro cm^2 .

At $443^{\circ}.5$ C. $\chi = 81,6$ Erg. pro cm^2 .

At the last mentioned temperature the salt commenced to decompose already distinctly, while O_2 was split off; at higher temperatures therefore the values of χ appeared to *increase* gradually by the generation of $KClO_4$ and KCl .

It was not possible therefore to investigate the values of the temperature-coefficients at higher temperatures; in every case however they seem to be rather small.

With SILVERNITRATE: $AgNO_3$, the value of χ is about 164 Erg. pro cm^2 . at 280° C; at 410° C. it is about 153.8 Erg. In this case the temperature-coefficient is also in the neighbourhood of 0.6 or 0.9, — this being a rather small value too.

§ 21. It is not my intention, to discuss now already the here mentioned data, nor to add the remarks, which are suggested thereby. It is better to postpone that task, until the complete experimental material now available will be published. The given instances may however prove, that the question: *how to measure the surface-tensions of liquids with great accuracy within a temperature-interval, from -80° C. to 1650° C.*, may be considered now as completely solved.

Groningen, May 1914.

Laboratory of Inorganic Chemistry
of the University.

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

II. Measurements of Some Aliphatic Derivatives. By Prof. Dr. F. M. JAEGER and M. J. SMIT. (Communicated by Prof. P. v. ROMBURGH).

§ 1. In what follows the data are reviewed, which were obtained by us in the study of a series of aliphatic derivatives after the method formerly described by one of us¹⁾.

With respect to the liquids here used, we can make the following general remarks. No product of commerce, not even the purest ob-

¹⁾ F. M. JAEGER, These Proceedings (1914).

tainable, can be esteemed suitable for this kind of measurements: the small traces of humidity already, which even the best chemicals always contain, are sufficient to make the results unreliable. Most of the organic liquids of commerce however seem to contain several admixtures, in small quantities or even larger quantities of water. We often obtained a first purification by distilling a small fraction from it, whose boiling point remained constant between 1° or 2° C. In several cases even this appeared not to be possible: in such case the preparation was dried during some days by means of anhydrous sodiumsulphate; then, if the special character of the substance did not forbid this, it was dried again during a long time by means of freshly sublimed phosphorpentoxide, after which the fractional distillation was tried again. Commonly it appeared to be possible, to separate from it a fraction, whose boiling point remained constant between 1° or 2° C. With some preparations we succeeded in drying them by means of metallic sodium. After very dry fractions, boiling within a few degrees, had been obtained in this way, they were once more distilled with a small flame only, or on the water-bath, under atmospheric or reduced (12—20 mm.) pressure; in this operation only the fraction, boiling *within an interval of 1 C.*, was used for further treatment. The liquid was then cooled during several hours in a closed vessel, by means of a mixture of salt and ice, or by a bath of solid carbon dioxide and alcohol. If it crystallized, a further purification was often possible by repeated freezing and decanting. Often a very thin layer of a solid substance (eventually of ice) was deposited at the walls of the vessel, the rest remaining liquid and transparent; the liquid portion was poured into a dry, clean vessel then, and the said operation repeated, till no solid layer any more appeared. If however the phenomenon continued to appear, the liquid was treated again at least during a week with fresh phosphorpentoxide, and the freezing repeated again and again. Finally the purified liquid was distilled once more under atmospheric or reduced pressure; only the fraction, boiling *within half a degree* was collected then for the measurements. It is hardly necessary to mention, that hygroscopical liquids were preserved and treated in a suitable manner. The thus obtained liquid was commonly only a very small fraction (10% or 20%) of the original commercial preparation; it must be remarked, that the observed boiling-temperatures often differed appreciably from the data, given in the literature, and in several cases appeared to be *lower* than those; — which perhaps can be explained by the fact, that in the distillations, described in the literature, the liquid was heated *too* rapidly.

In our experiments the speed of distillation often did not exceed about six drops every minute. In some cases, e.g. with *toluene*, it was impossible to distil from the product of commerce a fraction, fulfilling all conditions; in such cases the substance was prepared in some other way, e.g. the mentioned *toluene* by dry distillation of purified calciumphenylacetate; etc. In the series of compounds described, several were taken from the collection of scientific preparations of this laboratory; from these also only the small, constantly boiling fraction was used for our purpose.

§ 2. Notwithstanding the by no means negligible differences of the boilingpoints observed, the specific gravities of the liquids in most cases differed only slightly or not at all from the data, given in the literature. If this was the case, — and we always controlled this by some pycnometrical determinations at 25° C., — the specific gravities at other temperatures were calculated from the expansion-formulae eventually already determined. If the direct determination of d_{40}^{25} did not agree with the number, given in literature, or if the expansion-formula was not known accurately enough, three specific gravities, e.g. at 25°, 50°, and 75° C. or at a higher temperature, were determined pycnometrically, and from these determinations an empirical equation of the second degree with respect to t , was calculated. This is completely sufficient here, because the specific gravities were all abbreviated with three decimals: an account of the densities in more than three decimals, must be esteemed valueless here, with respect to the obtained accuracy of the measurements. With most liquids, the mean decrease of the specific weight for 1° C. does not differ largely from 0,001. For temperatures of — 70° and above 100° C. it was often necessary to extrapolate by the aid of the established empirical formulae; although conscious of the uncertainties, which are always connected with such extrapolations, we are of opinion that we have not introduced here in this way errors of appreciable amount, because for these values such an error could manifest itself only in the third decimal place, and dilatation of the liquids occurs ordinarily in so regular a way, that the probability of heavy errors is thus highly diminished by this circumstance.

Moreover another way was not available at this moment, if not with large sacrifice of time and labour.

§ 3. In the following the obtained results are collected in tables. For the value of 1 mm. mercury at 0° C., 1333,2 Dynes (45°), was calculated, and this value was used in all further calculations; in the tables all numbers for χ and μ are adjusted by the necessary corrections.

The graphical diagrams relate to the variation of the so-called "molecular" surface-energy μ with the temperature; in the same diagram analogous, homologous compounds or such, related by simple substitutions, are put together; this will be of practical use for the comparative considerations later to be given, and allows a rapid review of the behaviour. For the construction of the diagrams, not the numbers of the tables, but those following directly from CANTOR'S formula, are used; therefore the correction, necessary to derive the absolute value of μ from these readings by diminution, are indicated on each curve in the diagrams.

§ 4. Aliphatic Derivatives.

This series of measurements relates to the following aliphatic
Molecular Surface
Energy in Erg. pro cm².

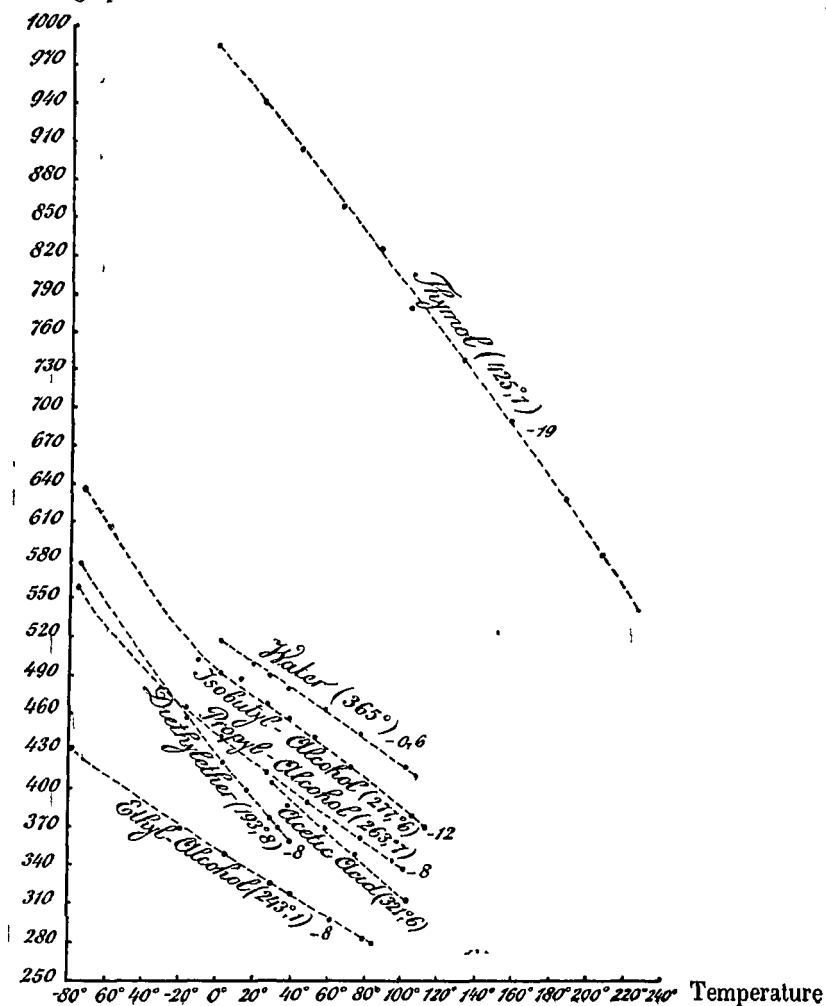


Fig. 1.

Substances: *norm. Propylalcohol*; *Isobutylalcohol*; *Diethylether*; *Ethylformiate*; *Ethylchloroformiate*; *Ethylacetate*, *Methyl*, *Ethyl*, and

I.

norm. Propyl-alcohol: $C_3H_7.OH.$					
Temperature in ° C	Maximum Pressure H		Surface-tension λ in Erg. per $cm^2.$	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro $cm^2.$
	in mm. mer- cury of 0° C.	in Dynes:			
-76°	1.170	1559.8	33.4	0.881	557.4
-21	0.924	1245.4	26.6	0.837	459.3
0	0.875	1167.3	24.9	0.820	435.9
25.5	0.807	1075.4	22.9	0.800	407.5
45	0.755	1006.4	21.4	0.784	386.0
74.5	0.679	905.3	19.2	0.759	353.9
90.6	0.638	850.2	18.0	0.746	335.6

Molecular weight: **60.06**. Radius of the Capillary tube: 0.04352 cm.
Depth: : 0.1 mm.

The substance boils at 96°7 C. constantly.

II.

Isobutyl-alcohol: $(CH_3)_2CH.CH_2OH.$					
Temperature in ° C	Maximum Pressure H		Surface tension λ 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			
-71.5°	1.149	1531.8	33.0	0.885	631.5
-12	0.890	1186.5	25.5	0.828	510.1
0.3	0.853	1137.2	24.4	0.817	492.5
10.4	0.825	1099.9	23.6	0.807	483.9
25.1	0.783	1044.5	22.4	0.794	460.9
35.1	0.756	1008.0	21.6	0.785	447.7
49.7	0.723	963.9	20.6	0.771	432.2
69.6	0.670	893.8	19.1	0.753	407.0
101	0.594	791.9	16.9	0.731	367.4

Molecular weight: **74.08**. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

The compound boils at 106°8 C. constantly; at the boilingpoint λ has the value: ca. 16.5 Erg. pro $cm^2.$

Isobutyl-Isobutyrate; Acetone; Methylpropylcetone; Ethyl-Acetyloacetate; Methyl-Methylacetyloacetate; Ethyl-Propylacetyloacetate; Methyl-, Ethyl-,

III.

Diethylether: $(C_2H_5)_2O$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension z 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			
-75°	0.990	1319.9	28.5	0.818	574.7
-20.5	0.748	997.2	21.5	0.758	456.2
0.2	0.670	893.8	19.2	0.735	415.8
10.9	0.628	837.2	17.9	0.723	392.0
25.3	0.584	778.6	16.7	0.707	371.2
29.5	0.574	766.2	16.4	0.703	365.9

Molecular weight: 74.08. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

The substance boils at $34.08^{\circ}C$. constantly; at the boilingpoint z is:
15.9 Erg. pro cm^2 .

IV.

Acetone: $CH_3.CO.CH_3$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension z 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			
-73°	1.236	1647.8	35.6	0.917	565.5
-19.5	0.971	1295.6	27.9	0.845	468.0
0.1	0.886	1181.3	25.4	0.818	435.4
11.4	0.838	1117.4	24.0	0.803	416.5
25.5	0.786	1047.9	22.5	0.785	396.4
35	0.740	985.6	21.1	0.772	375.9
50.1	0.695	926.6	19.8	0.757	357.4

Molecular weight: 58.05. Radius of the Capillar tube: 0.04385 cm.
Depth: 0.1 mm.

The boilingpoint is $56^{\circ}C$.; the value of z is there; 19.4 Erg.
pro cm^2 .

Propyl-, Butyl-, Isobutyl-, and Amyl-Cyanoacetates; Tri-, and Tetrachloro-methane; and Isobutylbromide.

V.

Methylpropylcetone: $CH_3 \cdot CO \cdot C_3H_7$.					
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. mercury of $0^{\circ}C$.	in Dynes			
-74.2	1.240	1653.2	35.4	0.936	721.4
-20.5	0.996	1327.9	28.3	0.872	604.6
0.3	0.913	1217.8	26.0	0.852	564.1
25.5	0.831	1107.6	23.6	0.826	522.7
45	0.762	1015.7	21.6	0.806	486.3
74.3	0.672	896.1	19.0	0.777	438.3
90.8	0.613	818.1	17.3	0.761	404.7
99.6	0.589	785.8	16.6	0.753	391.1

Molecular weight: 86.1. Radius of the Capillary tube: 0.04352 cm.
Depth: 0.1 mm.

The substance boils at $101.93^{\circ}C$. constantly.

VI.

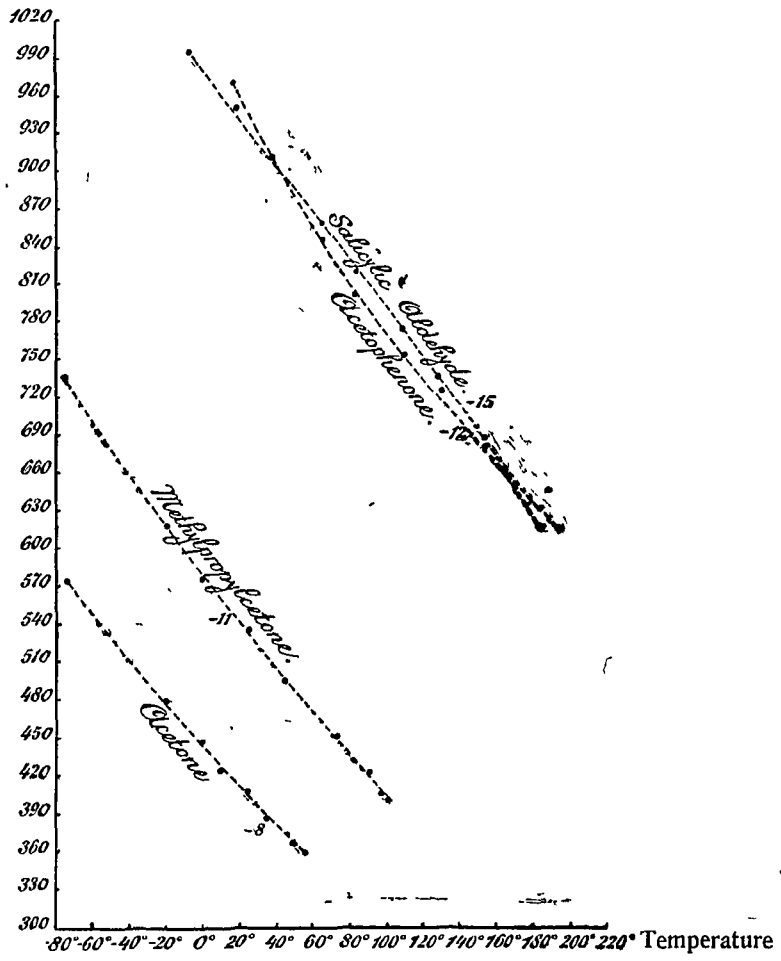
Ethylformiate: $HCO \cdot O(C_2H_5)$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension χ in Erg. pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy ν in Erg. pro cm^2 .
	in mm. mercury of $0^{\circ}C$.	in Dynes			
* -76.5	1.239	1661.2	37.8	1.032	502.7
* -16.2	0.945	1259.9	28.5	0.958	398.3
* 2.2	0.864	1151.9	26.0	0.938	368.5
24.9	0.802	1069.2	22.9	0.910	331.2
35.2	0.757	1009.6	21.9	0.899	319.3
49.2	0.718	957.2	20.5	0.879	303.4

Molecular weight: 50.05 Radius of the Capillary tube: 0.04408 cm.;
in the observations, indicated by *, this
radius was; $R = 0.04638$ cm.
Depth: 0.1 mm.

After carefully drying, this ether boils at $54.93^{\circ}C$. constantly; it
remains a relatively thin liquid as far as $-79^{\circ}C$. At the boiling-
point χ is 19.9 Erg. pro cm^2 .

Molecular Surface-
Energy in Erg pro cm².

Fig. 2.



VII.

Ethylchloroformiate: $Cl.CO.O(C_2H_5)$.					
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			
-75.5	1.353	1803.8	42.4	1.278	819.0
-21	1.046	1395.0	32.6	1.186	661.9
0	0.951	1269.2	29.6	1.160	609.9
25	0.847	1129.2	26.2	1.127	550.3
45.3	0.774	1031.8	23.9	1.095	511.7
70.2	0.692	922.6	21.2	1.050	466.8
84.8	0.643	857.8	19.8	1.022	443.9

Molecular weight: 108.49. Radius of the Capillary tube: 0.04803 cm.
Depth: 0.1 mm.

The compound boils at 91.95 C. constantly; at this temperature χ is 19.3 Erg. pro cm².

VIII.

Ethylacetate: $CH_3.CO.O(C_2H_5)$.					
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			
-74°	1.274	1698.5	36.6	1.016	716.8
-20	0.994	1325.2	28.4	0.949	582.1
0	0.892	1189.2	25.5	0.924	532.1
25.5	0.780	1039.9	22.2	0.893	473.8
34.7	0.744	992.5	21.2	0.881	456.6
55	0.679	897.2	19.1	0.856	419.3
70	0.623	838.5	17.8	0.829	399.2

Molecular weight: 88.06. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

After very carefully drying and repeated distillation, this ether boils at 77.91 C. constantly. It remains a thin liquid as far as -80° C. At the boilingpoint the value of χ is: 17.2 Erg. pro cm².

IX.

Methyl-Isobutyrate: $(CH_3)_2CH.CO.O(CH_3)$.					
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			
-73°	1.296	1728.0	37.1	0.995	813.1
-21.5	1.006	1341.9	28.7	0.936	655.1
0.5	0.903	1204.0	25.7	0.911	597.3
25.3	0.805	1073.2	22.8	0.882	541.5
45	0.727	969.7	20.6	0.859	497.9
74.7	0.631	840.9	17.8	0.825	442.0
91.3	0.589	785.8	16.6	0.806	418.6

Molecular weight: **102.08**. Radius of the Capillary tube: 0.04352 cm.
Depth: 0.1 mm.

The substance boils constantly at 91° 8 C.

X.

Ethyl-Isobutyrate: $(CH_3)_2CH.CO.O(C_2H_5)$.					
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			
-78°	1.165	1553.2	33.3	0.976	805.4
-21	0.940	1253.2	26.8	0.913	677.7
0	0.867	1155.9	24.6	0.891	632.3
25.2	0.779	1038.6	22.1	0.859	582.0
45	0.717	955.9	20.3	0.837	544.0
74.3	0.624	831.8	17.6	0.809	482.4
90.8	0.572	762.9	16.1	0.791	448.0
109.5	0.507	675.5	14.2	0.769	412.6

Molecular weight: **116.1**. Radius of the Capillary tube: 0.04352 cm.
Depth: 0.1 mm.

The substance boils at 110.° 2 C. constantly. At -76° C. it is again a thin liquid; it was only slightly turbid, probably by extremely fine crystals.

XI.

Isobutyl-Isobutyrate: $(CH_3)_2CH.CO.O(CH_2.(CH.(CH_3)_2).$					
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			
-76.5	1.182.	1576.3	33.8	0.951	960.6
-21.3	0.927	1236.2	26.4	0.896	780.8
0	0.865	1153.5	24.6	0.875	739.2
25.4	0.785	1047.8	22.3	0.850	683.1
45	0.731	974.3	20.7	0.830	644.2
74.7	0.638	850.2	18.0	0.801	573.6
91.1	0.596	795.0	16.8	0.784	543.1
109.2	0.545	726.1	15.3	0.766	502.3
134.5	0.469	625.0	13.1	0.740	440.1

Molecular weight: **144.11**. Radius of the Capillary tube: 0.04352 cm.
Depth: 0.1 mm.

The compound boils at 147.°2 C. constantly.

XII.

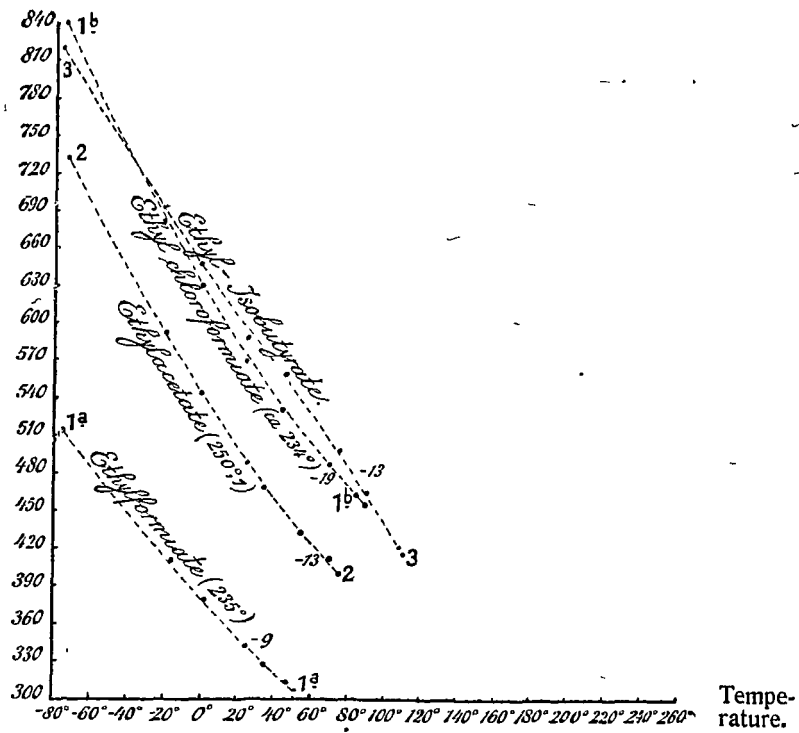
Ethyl-Acetyloacetate: $CH_3CO.CH_2.CO.O(C_2H_5).$					
Temperature in ° C.	Maximum Pressure H		Surface- tension γ in Erg. pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
-20°	1.210	1612.8	36.7	1.070	900.7
1	1.133	1510.5	34.3	1.048	853.5
* 25	1.113	1483.6	32.0	1.023	809.2
* 35.5	1.069	1424.7	30.7	1.013	781.4
* 49.5	1.024	1365.8	29.4	0.999	755.3
71	0.906	1207.4	27.3	0.976	712.3
89	0.841	1121.2	25.3	0.958	668.4
**125	0.774	1031.9	21.7	0.923	587.7
**153	0.675	900.2	18.9	0.896	522.1
**176	0.596	794.9	16.6	0.869	468.0

Molecular weight: **130.08** Radius of the Capillary tube: 0.04638 cm;
in the observations indicated by *, it was
0.04405 cm.; in those by **: 0.04352 cm.
Depth: 0.1 mm.

The substance boils at 179.°6 C. constantly.

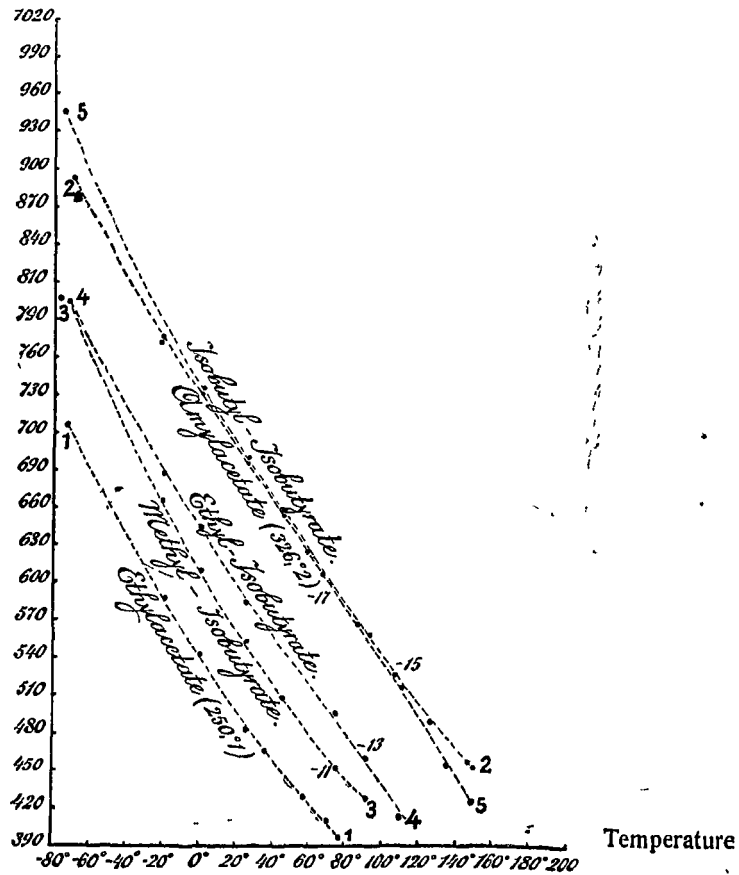
Molecular Surface-energy in Erg pro cm².

Fig. 3.



Molecular Surface-energy in Erg pro cm².

Fig. 4.



XIII

Methyl-Acetylmethylacetate: $CH_3CO \cdot CH(CH_3) \cdot CO \cdot O(CH_3)$.					
Temperature in ° 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° C.	in Dynes			
-71°	1.477	1969.6	46.5	1.121	1106.2
-21	1.218	1623.8	38.3	1.071	939.3
0	1.137	1515.7	35.7	1.050	887.2
25.3	1.046	1395.0	32.8	1.024	828.9
45.5	0.985	1313.2	30.8	1.003	789.2
70.2	0.901	1201.2	28.1	0.977	732.7
85.2	0.856	1141.2	26.7	0.962	703.4
117	0.768	1024.4	23.9	0.930	644.0
138.2	0.709	945.2	22.0	0.908	602.3
156	0.658	877.2	20.4	0.890	566.0

Molecular weight: 130.08. Radius of the Capillary tube: 0.04803 cm.
Depth: 0.1 mm.

Under a pressure of 18 mm., the substance boils at 75.°5 C.; in the at -71° C. very viscous liquid, the growing of the gas-bubbles took more than 60 seconds. The specific gravity at 25° C. is: $d_{40} = 1.0247$; at 50° C.: 0.9991; at 75° C.: 0.9732. At t° C.: $d_{40} = 1.0500 - 0.001006t - 0.00000024 t^2$.

XIV.

Ethyl-Propylacetyloacetate: $CH_3CO \cdot CH(C_3H_7)CO \cdot O(C_2H_5)$.					
Temperature in ° 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° C.	in Dynes			
-76.2°	1.430	1906.0	43.6	1.082	1280.1
-20	1.142	1522.2	34.8	1.007	1070.2
2.5	1.058	1410.1	32.2	0.978	1011.3
* 25	1.018	1356.6	29.4	0.948	942.7
** 35	0.977	1302.2	28.2	0.934	913.2
* 49	0.929	1238.7	26.8	0.916	879.2
70	0.818	1091.0	24.8	0.889	831.3
90.5	0.763	1017.7	23.1	0.866	786.8
* 125	0.714	951.5	20.2	0.833	706.0
* 143	0.669	891.5	18.9	0.816	669.7
* 152.9	0.641	854.8	18.1	0.806	646.7
* 177	0.576	767.5	16.2	0.785	589.1
* 200.5	0.507	676.4	14.2	0.764	525.8

Molecular weight: 172.13. Radius of the Capillary tube: 0.04638 cm.; in the observations indicated by *, R was 0.04352 cm.; in those indicated by **, it was 0.04408 cm. Depth: 0.1 mm.

Under ordinary pressure the boiling point is 223.°6 C. constantly; notwithstanding the great viscosity of the liquid at -76° C., it was yet possible here to determine the value of χ evidently very exactly, if the time of grow of the bubbles was sufficiently long (ca. 40 seconds).

XV

Methyl-Cyanoacetate: $CN \cdot CH_2 \cdot CO \cdot O(CH_3)$.					
Temperature in °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. mercury of 0° C.	in Dynes			
-76°	(2.424)	(3231.6)	(74.1)	1.222	(1387.8)
-16	1.443	1923.2	43.9	1.140	861.2
1	1.362	1815.4	41.4	1.122	820.8
** 25.5	1.337	1783.0	38.6	1.096	777.4
50;	1.184	1578.3	35.9	1.070	734.6
70.5	1.116	1487.7	33.8	1.039	705.4
90	1.043	1390.8	31.7	1.028	666.2
* 124.5	0.987	1315.8	28.0	0.994	601.8
* 153.1	0.877	1169.2	24.8	0.965	543.7
* 176.5	0.789	1052.4	22.3	0.942	496.8
* 197	0.713	951.3	20.1	0.921	454.6

Molecular weight: 99.05. Radius of the Capillary tube: 0.04638 cm.; in the observations indicated by *, R was: 0.04352 cm., in those with **, it was: 0.04408 cm.
Depth: 0.1 mm.

The carefully dried ether boils constantly at 203° C.; at -76° C. the liquid is extremely viscous and gelatinous; although the time of formation of the gasbubbles was about 100 seconds, the viscosity in this case evidently diminishes the exactitude of the determinations of γ . The specific gravity d_{40} was at 25° C.: 1.0962; at 50° C.: 1.0698; at 75° C.: 1.0438; at t° : $d_{40} = 1.1231 - 0.001086 t + 0.0000004 t^2$.

XVI.

Ethyl-Cyanoacetate: $CN \cdot CH_2 \cdot CO \cdot O(C_2H_5)$.					
Temperature in °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° C.	in Dynes			
-17°	1.313	1750.8	39.9	1.099	876.1
0	1.245	1660.2	37.8	1.082	838.6
** 25	1.222	1628.8	35.2	1.056	793.7
** 35.5	1.188	1583.5	34.2	1.046	776.1
49	1.083	1444.5	32.8	1.032	751.5
71	1.016	1354.0	30.7	1.009	713.6
90	0.951	1267.8	28.7	0.990	675.6
* 125	0.896	1194.8	25.4	0.955	612.4
* 153	0.803	1070.8	22.7	0.927	558.3
* 176	0.727	969.7	20.5	0.904	512.7
* 201	0.651	868.6	18.3	0.879	466.3

Molecular weight: 113.07. Radius of the Capillary tube: 0.04638 cm.; in the observations indicated by *, R was 0.04352 cm.; in those by **, it was: 0.04408 cm.
Depth: 0.1 mm.

The compound boils at 206° C. constantly; at -76° C. it becomes glassy and crystallizes very slowly on heating. The crystals melt at about -40° C. The specific gravity at 25° C. was: 1.0562; at 50° C.: 1.0307; at 75° C.: 1.0052; at t : $d_{40} = 1.0817 - 0.00102 t$, in general.

XVII.

Propyl-Cyanoacetate: $CN \cdot CH_2 \cdot CO \cdot O(C_3H_7)$.					
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			
-16°	1.236	1647.3	37.5	1.058	912.9
0	1.184	1578.3	35.9	1.042	882.9
** 25	1.164	1551.7	33.5	1.021	835.1
** 35	1.130	1506.5	32.5	1.011	815.5
** 51	1.075	1433.8	31.0	0.996	786.0
71	0.961	1280.7	29.1	0.976	747.6
114.5	0.834	1112.5	25.2	0.933	667.1
* 125.5	0.858	1144.4	24.3	0.923	647.9
* 152.5	0.780	1039.9	22.0	0.896	598.3
* 176.1	0.701	934.6	19.7	0.872	546.0
* 201	0.624	831.8	17.5	0.847	494.1

Molecular weight: 127.08. Radius of the Capillary tube: 0.04638 cm.; in the observations, indicated by *, the radius was: 0.04352 cm.; in those with **, it was: 0.04408 cm. Depth: 0.1 mm.

The substance boils at 216° C. constantly; at -79° it solidifies slowly to a crystal-aggregate, which melts at about -39° C. The density d_{40} was at 25° C.: 1.0214; at 50° C.: 0.9973; at 75° C.: 0.9717. at t° C.: $d_{40} = 1.0424 - 0.000962 t + 0.0000012 t^2$.

XVIII.

Butyl-Cyanoacetate: $CN \cdot CH_2 \cdot CO \cdot O(C_4H_9)$.					
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			
-21.3°	1.213	1617.5	35.2	1.041	928.8
0	1.159	1545.2	33.6	1.020	898.7
* 25.2	1.117	1489.0	31.7	0.998	860.3
* 45.2	1.055	1406.2	29.9	0.978	822.5
* 74.5	0.975	1300.6	27.7	0.952	775.8
* 94.1	0.924	1231.6	26.2	0.934	743.2
114.5	0.852	1135.3	24.6	0.915	707.4
135	0.797	1063.3	23.0	0.895	671.2
161.1	0.729	971.9	21.0	0.870	626.3
192.1	0.662	883.1	19.0	0.840	578.4
213.1	0.615	820.0	17.6	0.820	544.5

Molecular weight: 141.1. Radius of the Capillary tube: 0.04439 cm.; in the observations indicated by * it was: 0.04352 cm. Depth: 0.1 mm.

The ether boils at 230.5 C. constantly; it can be cooled as far as -80° C., without crystallisation setting in. The specific gravity d_{40} is at 25° C.: 0.9978; at 50° C.: 0.9749; at 75° C.: 0.9518; at t° it is: $d_{40} = 1.0204 - 0.000904 t + 0.00000016 t^2$.

XIX.

Isobutyl-Cyanoacetate: $CN \cdot CH_2 \cdot CO \cdot O(CH_2 \cdot CH \cdot (CH_3)_2)$					
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			
-20.5	1.179	1572.4	34.2	1.033	907.1
0.3	1.122	1495.9	32.5	1.014	872.7
* 25	1.069	1424.6	30.3	0.990	826.7
* 45	1.013	1351.1	28.7	0.971	793.3
* 74.8	0.934	1245.4	26.4	0.944	743.6
* 94.5	0.879	1174.6	24.9	0.925	710.9
115	0.811	1081.3	23.4	0.905	677.9
135.1	0.757	1009.2	21.8	0.886	640.5
161	0.686	914.6	19.7	0.862	589.5
191.8	0.595	792.9	17.0	0.834	520.0
213	0.541	720.9	15.4	0.815	478.4

Molecular weight: 141.1. Radius of the Capillary tube: 0.04439 cm.; in the observations indicated by *, R was: 0.04352 cm.
Depth: 0.1 mm.

The compound boils at 223° C. constantly; it can be undercooled as far as -76° C., and crystallizes then slowly into a crystalline aggregate, melting at about -26° C. The specific gravity at 25° C. was $d_{40} = 0.9903$; at 50° C.: 0.9669; at 75° C.: 0.9441. At t° it is generally: $d_{40} = 1.0138 - 0.000952 t + 0.00000032 t^2$.

XX.

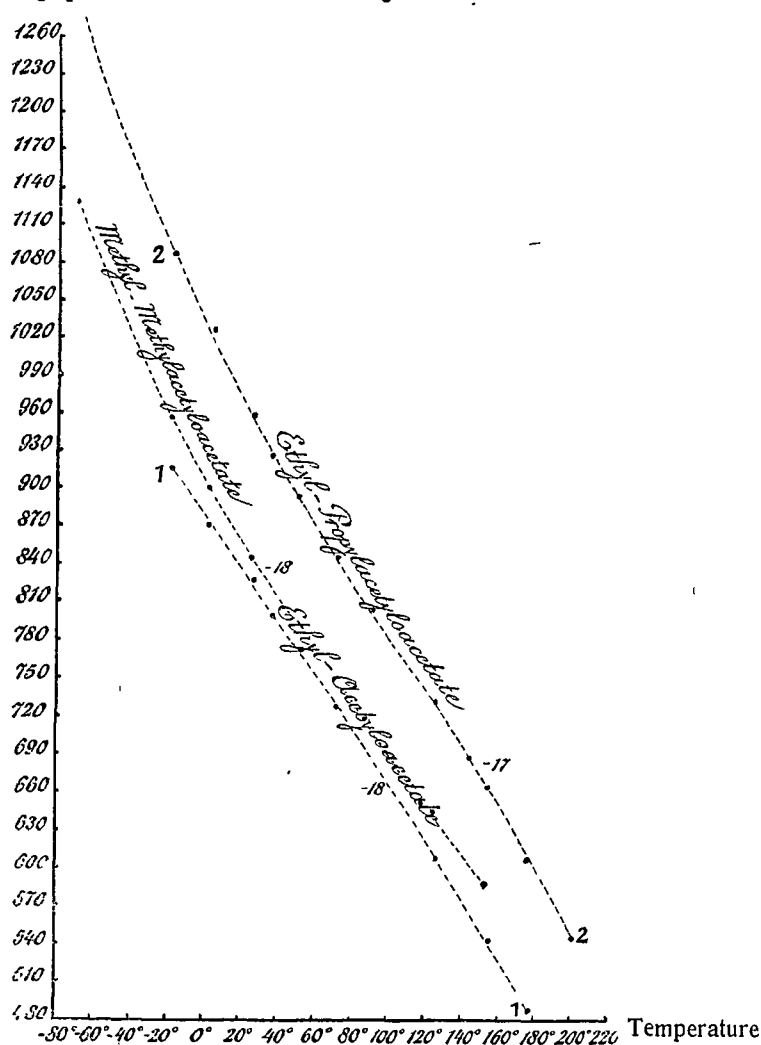
Amyl-Cyanoacetate: $CN \cdot CH_2 \cdot CO \cdot O(C_5H_{11})$					
Temperature in °C.	Maximum Pressure H		Surface- tension χ in Erg pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg pro cm ² .
	in mm. mercury of 0° C.	in Dynes			
-17.5	1.080	1440.3	32.7	1.017	933.5
1.5	1.029	1371.3	31.1	1.001	897.2
** 25.5	1.028	1370.2	29.5	0.976	865.5
** 35	1.000	1333.2	28.7	0.966	847.9
69	0.880	1172.9	26.5	0.939	797.8
89	0.831	1108.3	25.0	0.920	763.0
* 125	0.807	1075.4	22.7	0.891	707.7
* 153	0.744	992.6	21.0	0.864	668.3
* 176	0.689	919.1	19.4	0.843	627.6
* 201	0.634	845.6	17.8	0.821	586.1

Molecular weight: 155.11. Radius of the Capillary tube: 0.04638 cm.; in the observations indicated by *, R was 0.04352 cm.; in those with ** it was: 0.04408 cm.
Depth: 0.1 mm.

The compound boils at 240° C.; at -76° C. it is a jelly, but does not crystallize. The specific gravity at 25° C. was: $d_{40} = 0.9763$; at 50° C.: 0.9547; at 75° C.: 0.9327. At t° it is: $d_{40} = 1.0019 - 0.090061 t + 0.00000032 t^2$.

Molecular Surface
Energy in Erg. pro cm².

Fig. 5.



XXI.

Trichloromethane: $CHCl_3$.					
Temperature in °C	Maximum Pressure H		Surface- tension χ in Erg. pro cm ² .	Specific gravity $d_{4^{\circ}}$	Molecular Surface- energy ν in Erg. pro cm ² .
	in mm. mercury of 0° C.	in Dynes			
-22°	1.142	1523.4	32.5	1.555	587.5
0	1.050	1394.3	29.7	1.519	545.3
25	0.927	1236.0	26.2	1.476	490.4
35	0.881	1174.5	24.8	1.459	467.8
55	0.798	1063.9	22.4	1.425	429.2

Molecular weight: 119.51. Radius of the Capillary tube: 0.04385 cm.
Depth; 0.1 mm.

The trichloromethane was prepared from purest chloral, carefully dried, at -79° C. several times frozen, and purified by repeated distillation. It boils constantly at 61°2 C.; at this temperature, the value of χ is: 21,8 Erg. pro cm².

XXII.

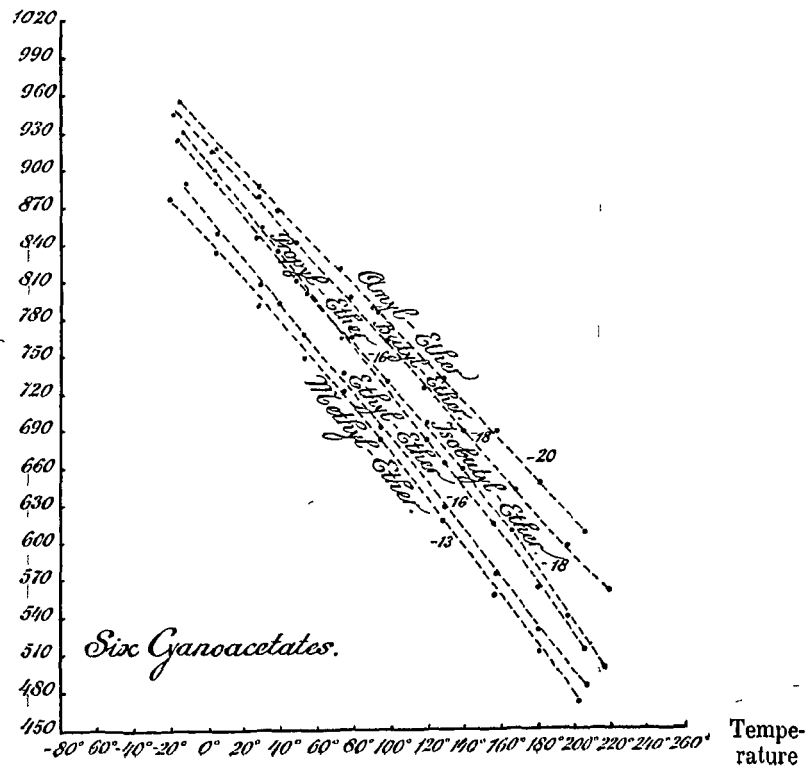
Tetrachloromethane: CCl_4 .					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension γ in Erg. pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg pro cm^2 .
	in mm. mer- cury of $0^{\circ}C$.	in Dynes			
-18°	1.087	1450.4	30.9	1.659	633.0
0.1	1.005	1340.9	28.5	1.632	590.2
25	0.899	1199.5	25.4	1.585	536.4
35	0.862	1149.4	24.3	1.560	518.6
55	0.793	1058.1	22.3	1.525	483.2

Molecular weight: 153.80. Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

Under reduced pressure (ca. 90 mm.) it boils at $26^{\circ}C$., and solidifies at $-60^{\circ}C$. to a white crystalline mass. Under ordinary pressure, it boils constantly at $76^{\circ}C$. At this temperature the value of γ is about: 20.2 Erg. pro cm^2 .

Molecular Surface-Energy
in Erg pro cm^2 .

Fig. 6.



XXIII.

Isobutylbromide: $(CH_3)_2CH \cdot CH_2Br$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension γ in Erg. pro cm ² .	Specific gravity d_4^{20}	Molecular Surface- energy ν in Erg. pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
-75°	1.227	1636.5	38.4	1.385	821.6
-19.5	0.949	1265.9	29.5	1.314	653.7
0	0.874	1166.0	27.1	1.291	607.6
25.4	0.790	1053.5	24.4	1.259	556.3
44.4	0.728	970.2	22.4	1.236	517.1
69.9	0.646	861.9	19.8	1.205	464.8
85.3	0.600	799.5	18.3	1.186	439.2

Molecular weight: 137.07. Radius of the Capillary tube: 0.04803 cm.
Depth: 0.1 mm.

The carefully dried compound boils very constantly at 90.5° C.; at this temperature γ is about 17.9 Erg. pro cm².

Molecular Surface-
Energy in Erg pro cm².

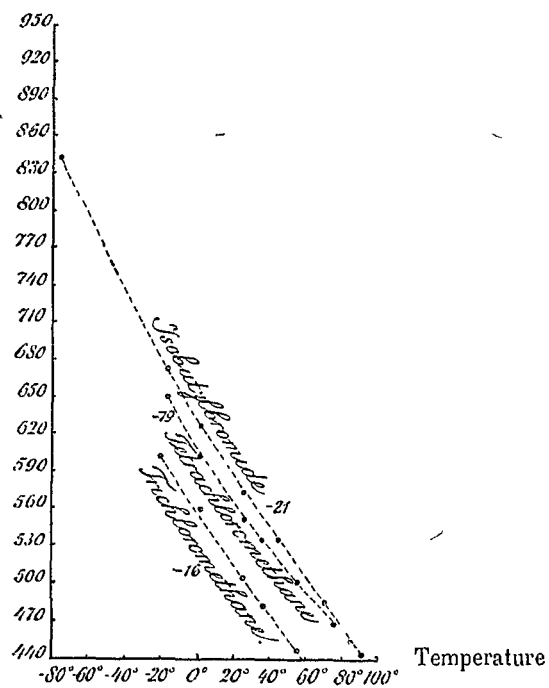


Fig. 7.

§ 5.- *Temperature-coefficients of μ of the here studied substances.*

<i>norm. Propylalcohol.</i>		<i>Isobutylalcohol.</i>	
<i>Temperature-interval:</i>	$\frac{\partial \mu}{\partial t}$ in Erg.	<i>Temperature-interval:</i>	$\frac{\partial \mu}{\partial t}$ in Erg.
between -76° and -21°	1,78	between -71° and -12°	2,3
-21° „ $+25^\circ$	1,11	-12° „ $+101^\circ$	1,1
25° „ 91°	1,10		
<i>Diethylether.</i>		<i>Ethylformiate.</i>	
between -75° and -20°	2,16	between $-76^\circ,5$ and -16°	1,72
-20° „ 0°	1,94	-16° „ $+25^\circ$	1,62
0° „ 29°	1,70	25° „ 35°	1,29
		35° „ 54°	1,12
<i>Ethylchloroformiate.</i>		<i>Ethylacetate.</i>	
between -75° and -21°	2,86	between -74° and 0°	2,50
-21° „ $+25^\circ$	2,41	0° „ 25°	2,37
25° „ 70°	1,82	25° „ 35°	1,86
70° „ 91°	1,70	35° „ 55°	1,78
		55° „ 77°	1,30
<i>Methyl-Isobutyrate.</i>		<i>Ethyl-Isobutyrate.</i>	
between -73° and $-21^\circ,5$	3,0	between -78° and $+109^\circ$	2,15
-21° „ $+25^\circ$	2,4		
25° „ 45°	2,1		
45° „ 91°	1,7		
<i>Isobutyl-Isobutyrate.</i>		<i>Acetone.</i>	
between -76° and -21°	3,2	between -73° and $-19^\circ,5$	1,81
-21° „ $+135^\circ$	2,18	-19° „ $+11^\circ$	1,66
		11° „ 54°	1,57
<i>Methylpropylcetone.</i>		<i>Ethyl-Acetyloacetate.</i>	
between -74° and 0°	2,13	between -20° and $+176^\circ$	2,19
0° „ 99°	1,73		
<i>Methyl-Methylacetyloacetate.</i>		<i>Ethyl-Propylacetyloacetate.</i>	
between -71° and -21°	3,39	between -76° and -20°	3,74
-21° „ 0°	2,47	-20° „ $+20^\circ$	2,84
0° „ 70°	2,18	25° „ 70°	2,36
70° „ 156°	1,94	70° „ 125°	2,24
		125° „ 153°	2,11
<i>Methyl-Cyanoacetate.</i>		<i>Ethyl-Cyanoacetate.</i>	
between -76° and -16°	not measurable independently of viscosity.	between -17° and $+201^\circ$	1,88
-16° „ $+197^\circ$	1,90		

Then an increase: 2,37 to 2,68, occurs as a consequence of beginning dissociation.

<p style="text-align: center;"><i>Propyl-Cyanoacetate.</i></p> <p>Temperature-interval: $\frac{\partial \mu}{\partial t}$ in Erg.</p> <p>between -16° and $+152^{\circ}$ 1,88</p> <p>Then an <i>increase</i>. 2.13, under dissociation and liberation of <i>HCN</i>.</p> <p style="text-align: center;"><i>Isobutyl-Cyanoacetate.</i></p> <p>between -20° and 0° 1,64</p> <p style="padding-left: 2em;">0° „ 115° 1,70</p> <p style="padding-left: 2em;">115° „ 213° 2,0</p> <p>Gradual decomposition, under liberation of <i>HCN</i>.</p> <p style="text-align: center;"><i>Chloroform.</i></p> <p>between -22° and $+55^{\circ}$ 2,06</p> <p style="text-align: center;"><i>Isobutylbromide.</i></p> <p>between -75° and -19° 3,0</p> <p style="padding-left: 2em;">-19° „ $+25^{\circ}$ 2,15</p> <p style="padding-left: 2em;">25° „ $69^{\circ},9$ 2,03</p> <p style="padding-left: 2em;">70° „ 90° 1,91</p>	<p style="text-align: center;"><i>Butyl-Cyanoacetate.</i></p> <p>Temperature-interval: $\frac{\partial \mu}{\partial t}$ in Erg.</p> <p>between -21° and $+213^{\circ}$ 1,62</p> <p style="text-align: center;"><i>Amyl-Cyanoacetate.</i></p> <p>between -17° and $+1^{\circ}$ 2,0</p> <p style="padding-left: 2em;">1° „ 201° ca. 1,6</p> <p style="text-align: center;"><i>Carbontetrachloride.</i></p> <p>between -18° and 0° 2,6</p> <p style="padding-left: 2em;">0° „ 25° 1,95</p> <p style="padding-left: 2em;">25° „ 55° 1,75</p>
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Evidently only in some cases the coefficient $\frac{\partial \mu}{\partial t}$ appears to be really constant; in most cases it *decreases* doubtless with a *rise* of temperature. Where the inverse behaviour was stated, a decomposition of the studied substance always seemed to occur. The value for $\frac{\partial \mu}{\partial t}$ is in the interval of ordinary temperatures relatively small for *propyl-* and *isobutyl-alcohol* and for the *ketones*; however in these cases it appears to be variable with the temperature in no higher degree than in the cases, where the values of $\frac{\partial \mu}{\partial t}$ do not differ largely from 2.0 Erg.

Groningen, June 1914.

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