The crystals are uniaxial and negative.

The optically active components are so highly soluble that it was impossible up to now, to obtain crystals suitable for measurements.

About the general conclusions, relating to the facts here described, vid. Publication I (March 1915) on this same subject.

Laboratory for Inorganic and Physical Chemistry of the University.

Groningen, March 1915.

Chemistry. — *"Investigations on the Temperature-Coefficients of the free Molecular Surface-Energy of Liquids at Temperatures from —80° to 1650° C."* **IX.** *The Surface-Energy of homologous Aliphatic Amines.* By Prof. F. M. JAEGER and Dr. JUL. KAHN. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of April 23, 1915).

§ **1.** During the continuation of our studies regarding the influence of special substitutions in the molecules on the specific and molecular surface-energy of homologous compounds, our attention was drawn to the fact, that the free surface-energy and its temperature-coefficient in the case of organic derivatives of the trivalent nitrogen often show remarkably low values. We therefore determined to study systematically a greater number of the homologous series of the aliphatic amines in the way previously described. The results of these investigations are communicated in the following pages.

A single determination of the value of the free surface-energy of carefully purified and dried anhydrous *ammonia*: NH_3 taught us that with this mother-substance itself, even at lower temperatures, the value of χ is a relatively small one.

We found at —73° C. for the specific surface-tension of liquid ammonia: about **37** Erg pro cm². [1]), a value considerably different from the sparsely published data in literature regarding the surface-energy of this liquid. As we had at the moment no means of maintaining constant lower temperatures for a longer time, we could not for the present continue these experiments further; however we hope to be able to return to these researches later on.

[1]) The radius of the capillar tube was: 0.04595 c.m., the depth of immersion: 0.1 mm. The maximum pressure observed was: 1.210 mm. of mercury of 0° C.

The 23 compounds of this homologous series studied here are: *Methyl-*, *Dimethyl-*, and *Trimethylamine; Ethyl-*, *Diethyl-*, and *Triethylamine; norm. Propyl-*, *Dipropyl-*, and *Tripropylamine; Isopropylamine; Allylamine*; *norm. Butylamine*; *Isobutyl-*, *Diisobutyl-*, and *Triisobutylamine*; *tertiary Butylamine*; *norm. Amylamine*, *Isoamyl-*, and *Diisoamylamine*; *tertiary Amylamine*; *norm. Hexyl-*, and *Isohexylamine*; *norm. Heptylamine*; while for the purpose of comparison the measurements of *Formamide* are reproduced here also.

The pure amines were first dried by means of metallic sodium or potassiumhydroxide, then fractionated in vacuo over *KOH*; because of the inevitable bumping of the liquid, the thermometer-readings oscillated within limits of about 2°.

The specific gravity must be determinated with most of these substances by means of a volumeter, because of their volatility and their tendency to attract carbondioxide and water-vapour from the atmosphere. Especially in the case of the lower-boiling amines these experiments appeared to be highly cumbersome and demanded much time; however we think the obtained results to be exact within about 0.1 %, which must be quite sufficient for the use here made of them.

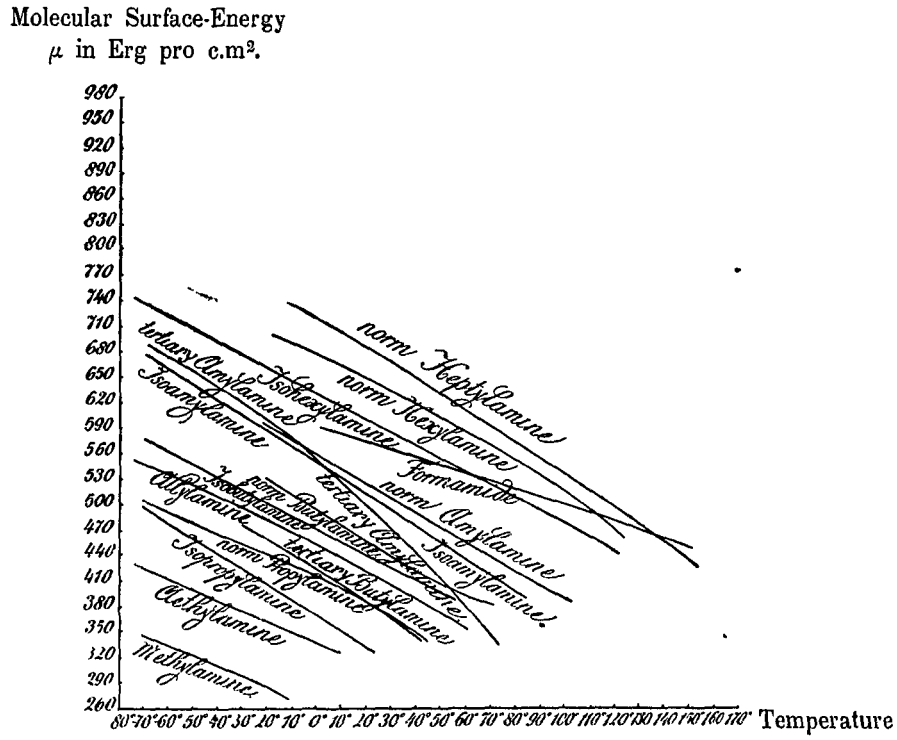

Fig. 1. Primary Amines.

§ **2.**

I.

Monomethylamine: $CH_3 . NH_2$.

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.
—70°	1.324	1764 8	29.2	0.759	346.7
—49	1.225	1633.2	26.5	0.736	321.2
—20	1.068	1423.9	23.0	0.705	286.9
—18	1.049	1399.8	22 7	0.702	283.9
—12	1.005	1340.1	21.7	0.696	272.9

Molecular weight: **31.05.** Radius of the Capillary tube: 0.03343 cm. Depth: 0.1 mm.

The dry amine boils under atmospheric pressure at —6° C. At —79° it is still a thin fluid mass, without any trace of beginning crystallisation. At the boilingpoint the value of χ can only slightly differ from: 20.9 Erg. pro cm².

The specific gravity was determined by means of a volumeter: at —79° C. it was: 0.7691; at 0° C. 0.6831. At $t°$ it may be calculated from: $d_{4°} = 0.6831 - 0.00109\, t$.

The temperature-coefficient of μ increases gradually at higher temperatures: between —70° and —20° C. it is: **1.20**; between —20° and —18° C. it is: **1.50**; and between —18° and —12°: **1.83** Erg. per degree.

II.

Dimethylamine: $(CH_3)_2 NH$.

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.
—78°	0.842	1121.4	25.2	0.757	384.2
—50	0.745	995.5	22.5	0.730	351.4
—23	0.672	897.0	20.2	0.703	323.5
0	0 606	807.9	18.1	0 680	296.4
5	0.586	783.5	17.7	0.675	291.3

Molecular weight: **45.06.** Radius of the Capillary tube: 0.04595 cm. Depth: 0.1 mm.

The liquid boils at +7.°5; at —76° C. it is not yet solidified. At the boilingpoint χ has the value: 17 5 Erg. per cm². The specific weight at 0° C. was: 0.6804; at —79° C : 0 758; at $t°$ C.: it is: $d_{4°} = 0\,6804 - 0\,0009886\, t$.

The temperature-coefficient of μ has a mean value of **1.10** Erg per degree.

III.

Trimethylamine: $(CH_3)_3N$.

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.
—73°	0.827	1102.5	24 8	0.748	456.6
—52	0.737	983 7	22 2	0.725	417.4
—32	0.678	897.8	20.0	0.704	383.5
—19	0 627	834 8	18 6	0.691	361.0
— 4	0.583	777 2	17.3	0.675	341.1

Molecular weight: **59 10.** Radius of the Capillary tube 0.04595 cm. Depth 0 1 mm.

The liquid boils at about —3° C.; even at —75° C. it was still as thin as water, and no trace of crystallisation could be observed. The specific gravity at 0° C was 0 6709, at —79° C 0 7537; at t° C is $d_{4°} = 0\,6709 - 0\,001048\ t$. The temperature coefficient of μ decreases slowly with rising temperature: between —73° and —52° C. it is: **1.89**; between —52° C. and —19° C.: **1.71**; and between —19° and —4° C · **1 33** Erg. per degree.

IV.

Ethylamine: $(C_2H_5)\ NH_2$.

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.
—74°	0.961	1281.2	29.1	0.785	433.1
—33	0 807	1078.1	24.6	0.741	380.5
—21.5	0.773	1030 6	23.4	0 729	365.9
0	0.709	945.2	21.4	0 708	341 1
9 9	0.676	901.2	20.4	0.698	328.4

Molecular weight: **45.07.** Radius of the Capillary tube: 0.04595 cm. Depth: 0.1 mm.

The amine boils at 20° C.; even at —76° it is liquid still. At the boiling-point γ is about: 19 9 Erg. pro cm². The specific weight at 0° C. was volumetrically determined to be: $d_{4°} = 0.708$ at 0° C; and 0 790 at —79° C. At t° C. it is: $d_{4°} = 0.7085 - 0\,001032\ t$.

The temperature-coefficient of μ is constant and **1.25** Erg. per degree.

V.

Diethylamine: $(C_2H_5)_2NH$

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.
21°5	0.765	1019 9	23.0	0.752	486.2
0	0.693	923 9	20.8	0.731	448.1
10	0 655	873 8	19.7	0 720	428.8
23.4	0.616	819 5	18.3	0 708	402 8
35	0.587	781 4	17.4	0.695	387.7
45	0 568	754.5	16 6	0 686	373.1

Molecular weight: **73.10.** Radius of the Capillary tube: 0.04595 cm. Depth 0.1 mm.

The amine boils at 56° C and crystallises at about —40° C. At the boiling-point γ possesses the value: 16 2 Erg. pro cm². The specific gravity at 0° C. was: 0 7315; at 25° C 0 7045; at 50° C. 0 677. At t° in general: $d_{4°} = 0.7315 - 0.00107\,t - 0\,0000001\,t^2$

The temperature coefficient of μ has a mean value of: **1.69** Erg. per degree.

VI.

Triethylamine: $(C_2H_5)_3N$.

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.
—70°	0.929	1238 5	28.1	0.816	698.5
—20.5	0.740	985.5	22.1	0 769	571.5
0	0.658	887.0	20.0	0.749	526.4
25.6	0.596	794.6	17.8	0.725	478.8
41.2	0.572	753.1	16 7	0 710	455.5
55 7	0.505	681.1	15.8	0 695	437.1
70.4	0.478	637.3	14.1	0.681	395.4
84.3	0.453	603.9	13.3	0 667	378.2

Molecular weight: **101.13.** Radius of the Capillary tube: 0.04676 cm. Depth: 0.1 mm.

The liquid boils under 762 mm. at 87° or 89° C. Even at —72° the amine is still a thin liquid The specific weight was determined volumetrically: at 0° C: it was: 0.7495; at 25° C : 0.7255; at 50° C : 0 701 At t° C: $d_{4°} = 0\,7495 - 0.00095\,t - 0\,0000004\,t^2$. At the boilingpoint γ has the value: 12.8 Erg.

The temperature-coëfficient of μ decreases gradually with increasing temperature: between —70° and —20° C it is: **2.56**, between —20° C and 0° C: **2.20**; between 0° and 26° C: **1.86**, and between 26° and 84° C: **1.71** Erg. per degree Celsius.

VII.

normal Propylamine: $C_3H_7NH_2$.

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°	0.951	1267.9	29.3	0.817	508.6
—21	0.795	1059.9	24.5	0.763	445.1
0	0.725	966.6	22.3	0.741	412.8
15	0.665	889.6	20.7	0.724	389.4
25.6	0.639	851.9	19 7	0.714	374.1
42	0.585	779.8	18.0	0.696	347.7

Molecular weight: **59.08.** Radius of the Capillary tube: 0.04676 cm. Depth: 0.1 mm.

The liquid boils under a pressure of 760 mm. constantly at 47.°5 C.; at —72° C. it is still very thin. The density at 0° C. is: 0,741; at 25° C.: 0,714; at 40° C.: 0.698. At $t°$ in general: $d_{4°} = 0.741 - 0.001075\,t$. At the boilingpoint the value of χ is: 17.5 Erg.

The temperature-coefficient of μ is fairly constant and equal to: **1.54** Erg. per degree.

VIII.

Dipropylamine: $(C_3H_7)_2NH$.

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.
*—19°.5	0.816	1087.9	25.7	0.775	661.0
* 0	0.746	994.6	23.5	0.756	614.6
29.9	0.652	878.0	20.4	0.728	547.1
48.3	0.596	795.4	18.4	0.712	500.8
65	0.546	728.5	16.8	0.696	464.2
80.9	0.505	674.0	15.6	0.682	434.2
104.5	0.453	603.9	13.8	0.662	394.3

Molecular weight: **101.10.** Radius of the Capillary tube: 0.04777 cm; in the measurements indicated by *, the radius was: 0 04839 cm. Depth: 0.1 mm.

Under a pressure of 762 mm. the liquid boils at 110.°5 C. Even at —78° C. it remained clear, but solidifies afterwards into a mass of white crystals, melting at —45° C. At the boilingpoint $\chi = 13.9$ Erg. pro cm². The specific weight at 0° C. was: 0.7565; at 25° C : 0.733; at 50° C.: 0 710. At $t°$ C. it is: $d_{4°} = 0.7565 - 0.00095\,t + 0.0000004\,t^2$. The temperature-coefficient of μ decreases gradually with increasing temperature: it is **2.38** between —20° and 48° C; between 48° and 65° C.: **2.19**; between 65° and 81° C : **1.89**; between 81° and 104° C.: **1.69** Erg.

IX.

Tripropylamine: $(C_3H_7)_3N$.

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°	0.977	1302.5	30.6	0.830	948.2
—20.5	0.816	1087.9	25.6	0.789	820.6
0	0.758	1010.4	23.6	0.773	766.9
25.6	0.693	923.9	21.5	0.753	710.9
40 5	0.647	862.6	20.1	0.741	671.8
55.5	0.607	810.5	18.8	0.729	635.2
80.2	0.545	726.6	16.8	0.709	578.3
92.2	0.513	684.4	15.8	0.699	549.0
116.1	0.460	613.5	14.1	0.680	499.0
*136	0.421	561.3	12.6	0.664	453.1
*149.5	0.385	513.9	11.5	0.653	418 2

Molecular weight: **143.18.** Radius of the Capillary tube: 0.04792 cm.; in the observations indicated by *, the radius was: 0.04670 cm.
Depth: 0.1 mm.

The amine boils constantly at 157° C. and 765 mm. pressure. Even at —79° it remains liquid. The specific gravity was determined with the aid of a volumeter: at 0° C. it was 0.773; at 25° C.: 0.753; at 50° C.: 0.733. At t° generally: $d_{4°} = 0\,773 - 0.0008\,t$. At the boilingpoint χ was about: **10.9** Erg.

The temperature coefficient of μ is fairly constant; its mean value is: **2 41** Erg. per degree.

X.

Isopropylamine: $C_3H_7NH_2$.

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.
—79°	0.929	1238.5	28.1	0.781	502.7
—10.5	0.734	975.7	21 8	0.728	408.7
5	0.636	852.0	19.4	0.709	370.1
1	0.596	794.6	17.7	0.694	342.6
25.2	0.564	751.9	16.8	0.684	328.3

Molecular weight: **59.09.** Radius of the Capillary tube: 0.04676 cm.
Depth: 0.1 mm.

The amine boils at 33 —35° C., under 760 mm. The specific gravity at 18° C. is: 0 691; the other values were calculated by adopting 0.001 as the mean temperature coefficient, which may not deviate much from the true value of it. At the boilingpoint χ has the value: 16.0 Erg.

The temperature-coefficient of μ is fairly constant, and in mean: **1.76** Erg. per degree Celsius.

XI.

Allylamine: $C_3H_5 . NH_2$.

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.
—75°	1.547	2064.0	34.2	0.867	557.5
—15	1.265	1687.1	27.9	0.801	479.5
0	1.180	1573.4	26.0	0.785	452.9
9.7	1.122	1495.7	24.7	0.777	433.2
20	1.072	1429.8	23.6	0.763	418.9
29.5	1.031	1376.0	22.7	0.752	406.9
40	0.979	1304.2	21.5	0.741	389.2
50.5	0 935	1245.1	20.5	0.730	374.8

Molecular weight: **57.07.** Radius of the Capillary tube: 0 03343 cm. Depth: 0 1 mm.

Under a pressure of 751 mm. the substance boils at 53° C. At the boilingpoint χ has the value of 20.6 Erg. pro cm². The specific gravity at 0° C. was: 0.785; at 25° C.: 0.757; at 50° C : 0.730. At $t°$ in general: $d_{4°} = 0.785 - 0\ 0011\ t$.

The temperature-coefficient of μ oscillates round a mean value of: **1.40** Erg. per degree.

XII.

normal Butylamine: $C_4H_9NH_2$.

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.
—21°	0 853	1137 6	26.1	0.785	536.2
0	0.779	1038.6	23.8	0.764	497.9
25.3	0.695	926 6	21.2	0.739	453.5
41	0.650	866.6'	19.7	0.723	427.5
55	0.606	808.4	18.4	0.709	404.6
70.8	0.574	765.2	17.4	0.693	388.5

Molecular weight: **73.1.** Radius of the Capillary tube: 0.04676 cm. Depth: 0 1 mm.

Under a pressure of 760.5 mm., the boilingpoint was 76° —78° C. The liquid crystallises in a bath of solid carbondioxide and alcool, and then melts at —46° C. At the boilingpoint χ has the value: 17 0 Erg. The specific weight at 0° C. is: 0 764; at 25° C : 0.739; at 40° C : 0.727. At $t°$ C.: $d_{4°} = 0.764 - 0.001\ t$.

The temperature-coefficient of μ decreases gradually with increasing temperature: between —21° and 0° C. it is: **1.82**; between 0° and 25° C.: **1.75**; between 25° and 55° C.: **1 64**; and between 55° and 71° C.: **1.02** Erg. per degree.

XIII.

Isobutylamine: $C_4H_9NH_2$.

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.
—70°	0.931	1243.5	28.9	0.812	580.5
—20.5	0.779	1038.5	24.0	0.771	499 0
0	0.730	973.2	22.4	0 750	474 4
25.3	0.666	887.9	20.4	0.724	442.3
41.8	0.626	831 2	18.8	0.706	414.5
55.8	0.574	761.0	17.7	0.692	395.5

Molecular weight: **73.10.** Radius of the Capillary tube: 0 04676 cm. Depth: 0.1 mm.

Under a pressure of 760.5 mm the amine boils at 67°—68° C. At —70° it is still liquid and not viscous. At 0 C. the specific weight was: 0.750; at 25° C.: 0.724; at 50° C: 0.698. At t° C it can be calculated from the formula: $d_{4°} = 0\ 7505 - 0\ 00104\ t$.

The temperature-coefficient of μ oscillates somewhat round a mean value of: **1.44** Erg. per degree.

XIV.

Diisobutylamine: $\{(CH_3)_2\,CH\,.\,CH_2\}_2$.

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.
—72°	0.994	1325.2	29.9	0.825	868.5
—22.5	0.838	1124.4	25.4	0.782	764.6
0	0.769	1026.4	23.2	0.763	709.9
10	0.731	974.9	21.9	0.754	675.5
23	0.691	924.0	20.7	0.743	644.8
35.2	0.660	879.9	19.7	0 733	619.2
45	0 634	842.8	18.8	0.724	595.8
56.7	0.605	802.6	17.8	0.714	569.3
63	0.583	775.2	17.2	0.709	552.7
* 80.9	0 515	686.6	15 9	0.693	518.8
* 104.5	0.459	611.9	14.1	0.673	469.1
* 125	0.408	544.3	12.5	0.656	423.1

Molecular weight: **129.16.** Radius of the Capillary tube: 0 04595 cm.; with the measurements, indicated by *, the radius was: 0 04777 cm. Depth: 0.1 mm.

Under a pressure of 760 mm. the amine boils constantly at 142° C. At —78° the liquid becomes very viscous, but does not crystallize. At the boilingpoint χ has the value: **11.3** Erg. pro cm². The density was volumetrically determined; it was found at 0° C.: 0 763; at 25° C.: 0.741; at 50° C.: 0.720. At t° therefore: $d_{4°} = 0.763 - 0.00086\ t$. The temperature-coefficient of μ is in general: **2.40** Erg. per degree.

6*

XV.

Triisobutylamine: $(C_4H_9)_3N$.

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.
—21°	1.026	1367.9	24.5	0.797	926.2
0	0.982	1309.1	23.4	0.782	895.9
20.5	0.932	1243.1	22.2	0.767	861.0
35.3	0.894	1191.9	21.3	0.757	833.4
50 5	0.862	1149.2	20.5	0.745	810.6
65.5	0.825	1100.1	19.6	0.733	783.5
75.5	0.798	1063.9	18.9	0.725	761.1
90.3	0.758	1010.6	18.0	0.713	732 9
99.8	0.726	968.1	17.2	0.704	706.3
115.1	0.684	911.9	16.2	0.692	672.9
124.5	0.652	869.2	15.4	0.683	645.3
139	0.612	814.0	14.4	0.672	610.0
155.8	0.563	751.0	13.3	0.654	573.6
170	0.519	693.0	12.2	0.640	533.9
185	0.471	627.0	11.0	0.626	488.5

Molecular weight: **185.26.** Radius of the Capillary tube: 0.03636 cm. Depth: 0.1 mm.

The amine boils under a pressure of 754 mm. constantly at 189° C. In a bath of solid carbondioxide and alcool it solidifies, and will melt afterwards at —24° C. At the boilingpoint the value of χ is: **10.6** Erg. The specific weight was determined by means of a volumeter: at 0° C. it was found: 0.782; at 25° C.: 0.764; at 50° C.: 0.745. At $t°$ generally: $d_{4°} = 0.782 - 0\,0007\,t - 0.0000008\,t^2$. The temperature-coefficient of μ increases gradually with rise of temperature: between —21° and 0° it is: **1.44**; between 0° and 100°: **1.86**; between 100° and 185° C. its mean value is: **2.61** Erg. per degree Celsius.

XVI.

tertiary Butylamine: $(CH_3)_3 . C . NH_2$.

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.
—30°	1.023	1364.0	22.5	0.747	477.8
—15	0.956	1274.5	21.0	0.732	452.0
0	0.884	1177.7	19.4	0.716	423.8
10	0 840	1120.2	18.4	0 706	405.7
20	0.797	1061.0	17.4	0 694	388.1
29.5	0.749	999.0	16.4	0.685	369.0
40.5	0.698	930.6	15.3	0.672	348.6

Molecular weight: **73 1.** Radius of the Capillary tube: 0.03343 cm. Depth: 0 1 mm.

The amine boils at 44° C. under a pressure of 757 mm. In a bath of solid carbondioxide and alcohol, it crystallizes readily at —54° C At the boiling-point χ has about the value: **14.9** Erg. pro cm². The density at 0° C. was: 0 716; at 25°: 0 689; at 40° C.: 0.672; in general at $t°$ C.: $d_{4°} = 0.716 - 0.001048\,t - 0\,000001\,t^2$. The temperature-coefficient of μ is between —30° and 0° C. about **1.85**; afterwards: **1.25** Erg. per degree.

XVII.

normal Amylamine: $C_5H_{11}NH_2$.

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.
—21°	0.861	1146.7	25.9	0.791	595.1
0	0.789	1054.7	24.1	0.770	563.5
25.5	0.730	973.2	21.9	0.746	523.2
41.2	0.669	895.3	20.4	0.731	494 0
55.5	0.641	858.1	19.2	0.718	470.5
70.9	0.601	800.7	17.9	0.705	444.1
85.0	0.568	762.1	17.0	0.692	427.0
99.8	0.526	701.1	15.6	0.681	396.0

Molecular weight: **87.11.** Radius of the Capillary tube: 0 04676 cm. Depth: 0 1 mm.

The liquid boils at 103°—104° C. under a pressure of 762 mm. At —79° it solidifies and crystallizes in needles, which melt at —38° C. The specific gravity was determined by means of a volumeter; at 0° C. it was found to be: 0.770; at 25° C.: 0.746; at 50° C.: 0 723. In general at t° C.: $d_{4°} = 0.770 - 0.00098\,t + 0.0000008\,t^2$.

The temperature-coefficient of μ has a mean value of **1.68** Erg. per degree.

XVIII.

Isoamylamine: $C_5H_{11}NH_2$.

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.
—69°	1.010	1346.5	30.9	0.840	682.1
—20 5	0.780	1042.0	25.9	0.791	595 1
0	0.779	1038.6	23.7	0.771	553.9
25.5	0.701	934.6	21.2	0.747	506.1
41.3	0.661	879.5	19.8	0.734	478.2
55.8	0.612	818.8	18.6	0.720	455.1
70.5	0.589	784.0	17.6	0.705	436.7
85.8	0.520	693 3	15.6	0.692	391.9

Molecular weight: **87.12.** Radius of the Capillary tube: 0.04676 cm. Depth: 0,1 mm.

Under a pressure of 761 mm. the amine boils at 95°—97°. At —72° C. it is still a thin liquid. The specific gravity at 0° C. was: 0.771; at 25° C.: 0 747; at 50° C: 0 724. At t° C. in general: $d_{4°} = 0.771 - 0.00098\,t + 0\,0000008\,t^2$.

The temperature-coefficient of μ oscillates somewhat round a mean value of **1.88** Erg. per degree.

XIX.

Diisoamylamine: $[(CH_3)_2 CH . CH_2 . CH_2]_2 NH.$

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.
*—20°	0.838	1117.2	26.5	0.801	894.9
* 0	0.778	1037.4	24.6	0.784	842.7
29.9	0.698	930.6	21.7	0.760	759.0
48.8	0.647	862.6	20.1	0.746	711.7
65	0.612	816.4	19.0	0.732	681.3
80.8	0.578	770.3	17.9	0.721	648.4
104.5	0.518	690.8	16.0	0.705	588.3
124	0 475	633.3	14.6	0 691	544.0
151.5	0.413	550.6	12.6	0.675	476.9
178.5	0 354	471.9	10.8	0.659	415.4

Molecular weight: **157 19.** Radius of the Capillary tube: 0.04777 c.m.; with the observations indicated by *, the radius was: 0.04839 c.m.
Depth: 0.1 m.m.

The liquid boils constantly at 188° C. and 760 m.m. In solid carbondioxide and alcohol the amine solidifies, and melts then at —44° C. At the boiling-point χ has the value: **10.2** Erg. pro cm². The specific weight was volumetrically determined; it was 0.784 at 0° C ; 0.764 at 25° C.; 0.745 at 50° C. At t° C. in general: $d_{4°} = 0.784 - 0.00084\, t + 0.0000008\, t^2$. The temperature-coefficient of μ has a mean value of: **2.37** Erg. pro degree.

XX.

tertiary Amylamine: $(CH_3)_2 (C_2H_5) C . NH_2.$

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.
—70°	1.252	1669.1	27.6	0.830	695.9
—19	1.101	1466 5	24.2	0.786	605.0
0	1.018	1357.2	22.4	0.756	554.7
9.5	0.983	1310.5	21.6	0.747	530.3
20	0.935	1245.1	20.5	0.736	498.2
29.3	0.895	1199.3	19.7	0.727	474.9
40.5	0.854	1138.5	18.7	0.716	446.3
50.5	0.812	1082.9	17.8	0.707	421.5
60	0.758	1011.0	16.6	0.697	383.0
70	0.709	945.2	15.5	0.688	344.9

Molecular weight: **87 11.** Radius of the Capillary tube: 0.03343 cm.
Depth: 0.1 mm.

Under a pressure of 757 mm. the amine boils at 76°.5 C. At —78° it is still a thin liquid, without any trace of crystallisation. At the boilingpoint χ has about the value: **15.0** Erg. The specific gravity was determined by means of a volumeter. At 0° C. it was: 0.756; at 25° C.: 0.731; at 50° C.: 0.707; at t° C. in general: $d_{4°} = 0.756 - 0.00102\, t + 0.0000008\, t^2$.

The temperature-coefficient of μ is between —70° and 50° C. fairly constant; its mean value is: **2.54** Erg. Above 50° it increases to about: **3.9** Erg.

XXI.

normal Hexylamine: $C_6H_{13} . NH_2$.

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.
—18°	1.171	1562 1	28.0	0.801	704.7
0	1.125	1499.8	26.9	0.785	686.2
20.4	1.058	1410.5	25.2	0.767	652.8
35.1	1.010	1347.6	24.1	0.754	631.5
50	0.956	1274.6	22.9	0.740	607.6
65	0.911	1215.6	21.7	0.725	583.7
74.8	0.884	1179.3	21.0	0.715	570.1
90.4	0.832	1109.2	19.8	0.700	545.2
99.8	0.795	1059 9	18.9	0.689	525.9
116	0 728	972.5	17.4	0.673	491.8
124.5	0.696	929.3	16.5	0.664	470 6

Molecular weight: **101.13.** Radius of the Capillary tube: 0.03636 cm. Depth: 0 1 mm.

The substance boils at 129°—130° C. under a pressure of 742 mm.; it solidifies in solid carbondioxide and alcohol and melts then at —19° C. At the boilingpoint χ has the value: 16.0 Erg. The specific gravity at 0° C. is: 0 7855; at 25° C: 0.763; at 40° C.: 0.749. At t° C.: $d_{4°} = 0.7855 - 0.00088\,t - 0\,0000008\,t^2$.

The coefficient of μ is originally small: about **1.03** between —18° and 0° C.; between 0° and 75° C. it is almost constant, with **1 55** Erg. as a mean value; above 75° C. it increases gradually from **1.55** Erg. to **2.50** Erg. per degree.

XXII.

Isohexylamine: $(CH_3)_2 CH . CH_2 . CH_2 . CH_2 NH_2$.

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.
—75°	1.397	1862.5	30.8	0.840	751.0
—20.8	1.203	1603.8	26.5	0.798	668.6
0	1.126	1501.6	24.8	0.780	635.3
10	1.096	1461.2	24.1	0.771	622.2
20	1.074	1430.2	23.3	0.762	606.3
29.8	1.021	1359.7	22.5	0.754	589.5
40.5	0.991	1321.2	21.8	0.744	576.3
60	0.924	1231.9	20.3	0.724	546.5
70	0.894	1191.9	19.6	0.716	532.1
80	0.861	1148.6	18.9	0.707	516.9
90	0.828	1103.9	18.1	0.698	499.3
100	0.795	1059.9	17.4	0.686	485.6
110.2	0.765	1019.9	16.7	0.676	470.6
121	0.726	969.1	15.9	0.665	453.0

Molecular weight: **101.13.** Radius of the Capillary tube. 0.03343 cm. Depth: 0.1 mM.

The amine boils at 123° C. under a pressure of 751 mm. Even at —79° it is still a thin liquid. At the boilingpoint the value of χ will be about: 15.8 Erg pro cm². The specific gravity was determined by the aid of a volumeter; at 0° C. it is: 0.780; at 25° C.: 0.758; at 50° C.: 0.735. At t° generally: $d_{4°} = 0.780 - 0.00086\,t - 0.0000008\,t^2$. The temperature-coefficient of μ oscillates round a mean value of: **1.51** Erg. per degree.

XXIII.

normal Heptylamine: $C_7H_{15}NH_2$.

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.
−18.5°	0.902	1202.4	27.5	0.804	752.8
0	0.857	1142.5	26.1	0.787	724.7
25.3	0.793	1057.2	24.1	0.765	681.9
41.5	0.744	993.0	22.7	0.750	650.9
56	0.714	950.8	21.5	0.737	623.7
70.9	0.663	886.2	20.3	0.723	596.4
84.5	0.634	845.2	19.1	0.711	567.5
100	0.607	809.2	18.3	0.697	551.0
*115.2	0.541	724.1	17.0	0.684	518.3
*130.8	0.545	723.8	15.7	0.669	485.8
*145.5	0.507	673.2	14.4	0.657	451.0

Molecular weight: **115.15.** Radius of the Capillary tube: 0.04676 cm.; in the measurements indicated by *, this radius was: 0.04529 cm.
Depth: 0.1 mm.

Under a pressure of 761 mm. the amine boils at 152°—154° C. The liquid can be undercooled, but finally solidifies in a bath of carbondioxide and alcohol into a colourless crystal-aggregation, melting at —18° C. Above 130° a slow decomposition is observable. At 0° C. the density is: $d_{4°} = 0.7875$; at 25° C.: 0,7650; at 40° C.: 0.7515. At t° C. it can be calculated from the formula: $d_{4°} = 0.7875 - 0.0009\,t$.

The temperature-coefficient of μ increases gradually at higher temperatures: between —18° and 0° C.: **1.52** Erg.; between 0° and 25° C.: **1.69**; between 25° and 71° C.: **1.87**; and between 71° and 145°: **1.96** Erg. per degree, as a mean value.

XXIV.

Formamide: $HCONH_2$.

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.
*0°	1.875	2499.7	59.6	1.167	596
29.9	1.806	2407.3	56.6	1.136	566
48.1	1.755	2340.3	55.1	1.120	551
65	1.702	2269.2	53.4	1.107	534
80.7	1.661	2214.8	52.1	1.094	521
104.5	1.598	2131.0	50.1	1.080	501
123.2	1.551	2068.2	48.6	1.071	486
152	1.460	1946.8	45.7	1.058	456

Molecular weight: **45 03.** Radius of the Capillary tube: 0.04777 cm.; in the observations indicated by *, the radius was: 0 04839 cm.
Depth: 0.1 mm.

Under a pressure of about 18 mm., the liquid boils at 114°. In a freezing mixture it solidifies into an aggregate of white crystals, which melts at —5° C. Above 145° C. a gradual decomposition under development of gas-bubbles, is observed; the χ-t-curve then rapidly falls towards the t-axis.

§ **3**. The results obtained are reviewed in the Tables I—XXIV above, while the relations of the corresponding μ-t-curves can be seen from the fig. **1—3**.

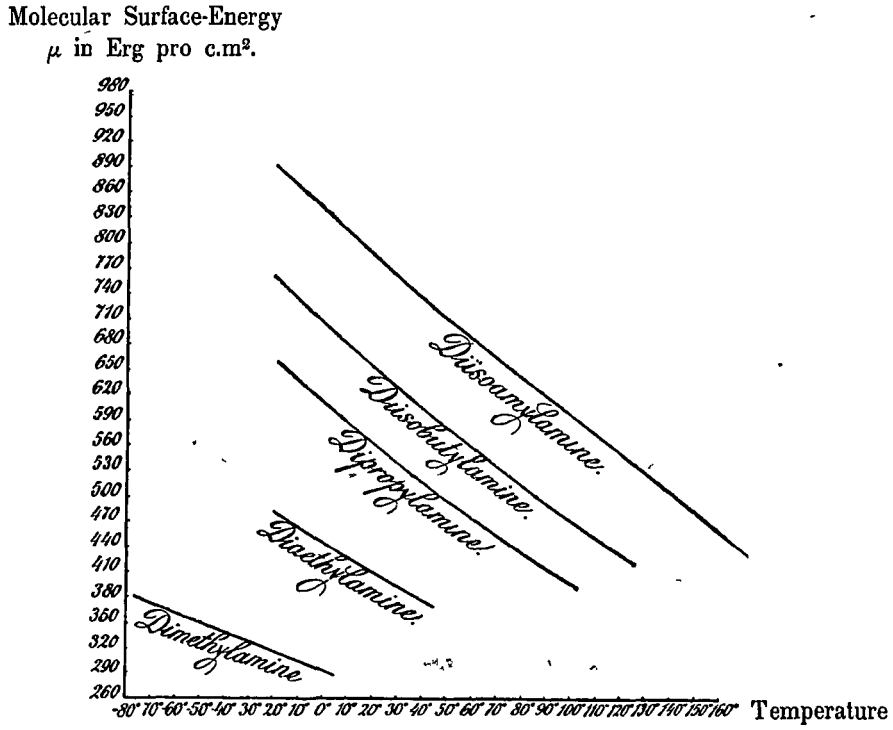

Fig. 2. Secondary Amines.

From these experiments it appears in the first instance, that the substitution of H-atoms in the ammonia-molecule by hydrocarbon-radicals, makes the surface-energy of the liquid compounds at the same temperatures increase regularly; and that, — pecularities left out of question, — that increase goes in general parallel to the augmentation of the number of C- and H-atoms. That however, even with the same number of C- and H-atoms, the special configuration of the molecule plays an important rôle in this, can soon be seen: e. g. the μ-t-curves for $(C_3H_7)NH_2$ are not only situated above those for $(CH_3)_3N$, etc., but it is also quite clear from fig. **1—3** *that generally in the case of correspondingly built-up isomer amines, those with normal- hydrocarbon-chains generally possess at any temperature a greater surface-tension than those with ramified hydrocarbon-chains; and that generally the surface-tension of such isomerides under the same conditions appears to be the lower, the more ramified the hydrocarbon-chains are* (e.g. *butyl-*, *isobutyl-*, and 3^{ary} *butyl-amines*; in the same way the corresp. *amylamines* between 10° and 70°; etc.)

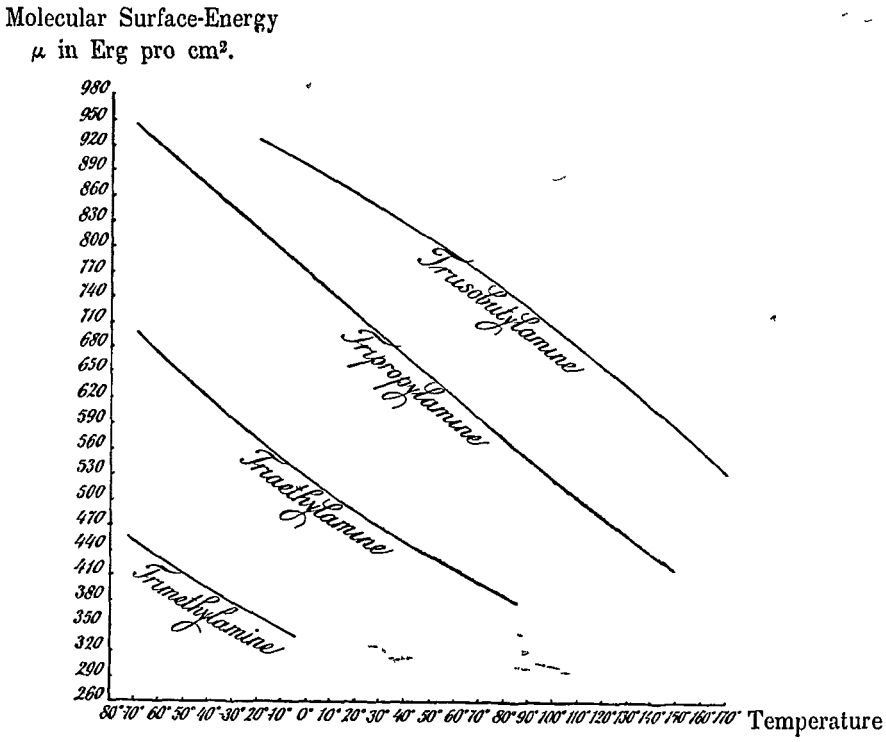

Fig. 3. Tertiary Amines.

On a comparison of the primary, secondary and tertiary amines of the same alkyl-radical, it appears that *the temperature-coefficients of μ are often analogous for* 1^{ary} *and* 3^{ary} *amines, but smaller than those for the* 2^{ary} *amines.*

However it becomes also clear, that a direct comparison of the *μ-t*-curves with the aim of studying the influence of the substitution by hydrocarbon-radicals in homologous compounds, may properly be made only in the case of amines of the same fundamental configuration; as e.g. by comparison of all primary, or all secondary, resp. tertiary amines, with each other. (fig. 1, 2 and 3). Really then the regular increase of the values of μ in these cases, if substitution occurs by more complicated hydrocarbon-radicals, comes to the fore in a most striking way.

With respect to the temperature-coefficients of μ it may be remarked that these generally appear rather *small*; the smallest values being present in the case of *primary* amines (1.2—1.8), while in the case of secondary amines these values are often somewhat greater (1.7—2.3), and just as with the tertiary amines, approach gradually to the values observed with other organic compounds. However, these rules are not without exceptions: e.g. in the case of *di*methylamine the

value of $\frac{\partial \mu}{\partial t}$ appears beyond doubt to be *smaller* than with *mono*-methylamine.

Finally the increase of the surface-energy by substitution of *H*-atoms also appears here, as formerly stated, to be appreciably greater if substitution occurs by *unsaturated*, than by saturated hydrocarbon-radicals: a comparison of the data for *allylamine* on the one side, and of *propyl-*, and *isopropylamine* on the other side, soon convinces of the truth of this.

Lastly we may draw attention here to the data regarding the *formamide*, which are also reproduced among those of the derivatives of trivalent nitrogen. Although this compound does not possess more than a single *C*-atom, the value of μ nevertheless appears here to be much greater than e.g. for $(CH_3)NH_2$, demonstrating the special influence of the strongly electronegative oxygen-atom, and more especially of the unsaturated carbonyl-radical, in a perfectly clear way.

Moreover this liquid, which in several respects shows some analogy with the strongly dissociating solvents, appears to possess a *very small* temperature-coefficient $\frac{\partial \mu}{\partial t}$: on an average about 0.89 Erg. per degree. It would be of interest to study the behaviour of inorganic salts if dissolved in this liquid, with respect to the electric current. In analogy to the case of water, one would be inclined to conclude in this case from the exceptionally small value of $\frac{\partial \mu}{\partial t}$, that the liquid formamide might be highly associated.

Laboratory for Inorganic and
Groningen, April 1915. *Physical Chemistry of the University.*

Chemistry. — "*The Allotropy of Sodium.*" I. By Prof. ERNST COHEN and Dr. S. WOLFF.

(Communicated in the meeting of April 23, 1915).

1. Some time ago ERNST COHEN and G. DE BRUIN [1]) relying on the determinations by EZER GRIFFITHS [2]) of the true specific heat of sodium, proved that this metal shows allotropy and that the substance known hitherto as "sodium" is a metastable system in consequence of the simultaneous presence of α- and β-sodium.

[1]) These Proc. **23**, 896 (1915).
[2]) Proc. Roy. Soc. London **89**, (A) 561 (1914).