If now it is once more remembered that $\mu = \chi . v^{2/3}$, it must be clear, that the cause of this phenomenon can only be found in the supposition, that v is *no* longer a comparable thing in these series of homologous salts. A suspicion arises more particularly that it is no longer permissible to take in account for the molecular weight M during the calculation of $v = \frac{M}{d}$, the values, following from the mere chemical formula of these salts. The significance of this would become evident, if one could suppose, that the *degree of dissociation* α of every one of these salts is a *different* one at the *same* temperature. Thus an indirect indication would be found here for the decision of the problem not solved completely up to this date; if molten salts must be considered to be electrolytically dissociated only *partially* or *totally*; and more particularly this question would be definitively answered in favour of the *partial* dissociation, when $\alpha < 1$. In how far this conclusion with respect to this fundamental problem may be considered to be justified, we also hope to discuss shortly in a second way, in connection with experimental data of another kind.

Groningen, Holland, June 1916.

Laboratory for Inorganic and Physical Chemistry of the University.

Chemistry. — "*Investigations on the Temperature-Coefficients of the Free Molecular Surface-Energy of Liquids between* — 80° *and* 1650° *C.* **XVI**. *The surface-tension of some Halogenides of Sulphur, Phosphorus, Arsenic, Antimony and Bismuthum*". By Prof. Dr. F. M. JAEGER and Dr. JUL. KAHN.

(Communicated in the meeting of June 24, 1916).

§ 1. In the following paper the measurements of the surface-energy are described, which were made with the substances: *sulphurmonochloride*; *phosphorustrichloride*; *phosphorustribromide*, *phosphorustriiodide*; *arsenictrichloride*; *arsenictribromide*; *antimonytrichloride*; *bismuthumtrichloride*, and *bismuthumtribromide*. In the case of *antimony-tribromide* on heating already immediately a decomposition was observed, the measurements were therefore no longer continued. The determination of the specific gravity of PI_3 appeared not to be possible with the desired accuracy owing to the too rapidly occurring decomposition of the substance under the influence of the water-vapour of the atmosphere.

§ 2.

1.

Sulphurmonochloride: S_2Cl_2.

Temperature in ° C.	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg per cm²
	in mm. mercury of 0° C.	in Dynes			
0°	1.641	2187.9	45.4	1.709	836.1
25.4	1.513	2017.9	41.8	1.670	781.7
50.1	1 379	1838.8	38.0	1.631	721.9
75	1.259	1678.4	34.6	1.591	668.3
90 5	1.198	1598.3	32.9	1.568	641.7
105.4	1.139	1518.1	31.2	1.544	614.8
121	1 075	1433.2	29.4	1.519	585.7

Molecular weight: **135.06.** Radius of the Capillary tube: 0.04242 cm. Depth. 0 1 mm.

The dark yellow liquid boils under atmospheric pressure at 138° C. At the boilingpoint χ has a value of about: **29.0** Erg The specific weight at 0° C. is 1.7094; at 138°.1 C.: 1.4920 (THORPE).

The temperature-coefficient of μ is originally, up to 50° C. about: **2,24** Erg; afterwards it diminishes to about **1.79** Erg. per degree.

2.

Phosphorustrichloride: PCl_3

Temperature in ° C.	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy μ in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			
—70°	1.574	2098.4	37.4	1.744	687.4
—20.5	1.332	1776.6	31.6	1.653	601.9
0	1.237	1650.2	29.3	1.613	567.3
20.8	1.155	1540.0	27.3	1.574	537.2
35 2	1.093	1457 6	25.8	1.547	513.6
50.3	1.031	1375.0	24.3	1.518	489 9
64.8	0.973	1298.1	22.9	1.492	467.0
75.1	0.932	1243.0	21.9	1.475	450.1

Molecular weight: **137.42.** Radius of the Capillary tube: 0.03636 cm. Depth: 0.1 mm.

The chloride boils under a pressure of 749 mm. at 75° C. Even at —75° C. it is again a thin liquid, but solidifies, according to TIMMERMANS, at —90° C. At the boilingpoint γ has the value: 21.9 Erg. The specific gravity at 16°.4 C. is: 1,582; at 46 .2 C.: 1,527; the critical temperature is: 290° C. (RAMSAY and SHIELDS). The temperature-coefficient of μ is relatively small: about **1,61** Erg per degree, as a mean value.

3.

Phosphorustribromide: PBr_3.

Temperature in ° C.	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy γ in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			
—20°	1.939	2585.2	45.8	2.972	927.0
0	1.894	2525.1	44.7	2.923	914.8
20.8	1.831	2441.0	43.2	2.871	894.7
35.3	1.795	2392.8	42.3	2.837	883.0
50.3	1.749	2332.2	41.3	2.799	870.0
64.8	1 699	2266.2	40.1	2.762	852.2
75.7	1.650	2200.2	38.9	2.735	832.1
90	1.574	2098.4	37.0	2.701	798.1
99.8	1.526	2035.2	36.0	2.676	781.4
116	1.438	1916.9	33.8	2.636	741 0
125	1.386	1848.1	32.6	2.615	718.5
140	1.295	1727.1	30.4	2 577	676.6
154	1.213	1617.1	28.4	2.542	637.9
170	1.126	1501.7	26.3	2.502	597.0

Molecular weight: **270.6.** Radius of the Capillary tube: 0.03636 cm. Depth: 0.1 mm.

Under a pressure of 750 mm. the compound boils at 170° 2 C The bromide solidifies at —50° C., and melts again at —40° C. At the boilingpoint γ has the value **26.2** Erg.

The temperature-coefficient of γ increases gradually: between —20° and 50° it is: **0.81** Erg; between 50° and 65° C.: **1.22**; between 65° and 76° C.: **1.84**; between 76° and 100°: **2.03**; between 100° and 170°: **2.63** Erg; etc. The specific gravities were calculated from the data given in literature by interpolation.

4.

Phosphorus-Triiodide: PJ_3.

Temperature in °C.	Maximum Pressure H		Surface-tension γ in Erg. per cm².
	in mm. mercury of 0° C.	in Dynes	
75.3°	1.999	2665.3	56.5
90 9	1.962	2616.9	55.5
105.5	1.931	2574.4	54.6
121.4	1.898	2530.4	53.6
135.5	1.852	2469.1	52.4
150	1.817	2423.4	51.4

Molecular weight: **411,8.** Radius of the Capillary tube: 0.04242 cm. Depth: 0.1 mm.

The red crystals melt at 55°—60° C.; the compound sublimes rapidly and is so easily attacked by water, that measurements of the specific weight are almost impossible.

5.

Arsenicumtrichloride: $AsCl_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension γ in Erg. per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy γ' in Erg. per cm².
	in mm. mercury of 0° C.	in Dynes			
—21°	1.842	2453.8	43.8	2.245	818.4
0	1.708	2277.2	41.4	2.205	782.9
20.8	1.629	2167.2	39.4	2.165	754.3
35.3	1.601	2134.4	38.0	2 136	734.0
50.2	1.544	2057.3	36.6	2.105	713.9
64.8	1.480	1976.2	35.1	2.073	691.7
75.7	1.445	1924.4	34.2	2.051	678.8
90	1.354	1805.6	32.8	2·016	658.5
110	1.312	1749.0	31.0	1.968	632.4

Molecular weight: **181.34.** Radius of the Capillary tube. 0.03636 cm. Depth: 0.1 mm.

The chloride boils at 130°5 C. under a pressure of 757 mm.; its melting-point is —13° C. The specific gravity was calculated from the formula $d_{4°} = 2.2050 - 0.001856\,t - 0.0000027\,t^2$, derived from the values given in literature. At 0° C. the density is 2,2050; at 20° C.: 2.1668; at 130°.2 C.: 1.9181. The temperaturecoefficient of γ' has a mean value of: **1.40** Erg per degree.

6.

Arsenicumtribromide: $AsBr_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy γ' in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			
49°.6	1 822	2429.1	49.6	3.328	1029.5
74.5	1.714	2285.1	46.6	3.261	980.5
90	1.647	2188.1	44.8	3 234	947.8
105.5	1.587	2116 9	43.0	3.184	919 3
121	1.518	2023.8	41.0	3.143	884.1
135	1.467	1956.6	39.6	3.111	859 8
149.6	1.417	1889.1	38.2	3.076	835 6
*165	1.273	1697.6	37.0	3.041	815.6
*179 7	1.244	1658.3	36.1	3.008	801.6

Molecular weight: **314,72.** Radius of the Capillary tube: 0,04242 cM.; in the observations indicated by *, it was: 0.04583 cm. Depth: 0.1 mm.

Under a pressure of 20 mm. the substance boils at 109° C.; the melting-point is 31° C. At 50° C. the specific gravity was; 3.3282; at 75° C.: 3 2623; at 100° C : 3.1995. At t° C.: $d_{4°} = 3\,3972 - 0\,002822\ (t - 25°) + 0.00000248\ (t - 25°)^2$.

The temperature-coefficient of γ' is up to 120° C. fairly constant; its mean value is **2,05** Erg per degree. Afterwards it decreases gradually, and becomes about **0,98** Erg at 180° C.

7.

Antimonytrichloride $SbCl_3$.

Temperature in ° C	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy γ in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			
74°.5	1.803	2403.7	49.6	2.672	957.4
90.4	1.739	2319 6	47.8	2.639	930.3
105	1 678	2242 5	46.0	2.606	902.8
120.6	1.616	2148 0	44.3	2.571	877.3
137	1.556	2074.4	42.6	2.534	851.8
149.8	1.506	2008.4	41.2	2.505	830.2
*165	1.342	1789.2	39.6	2.471	805.2
*178	1.299	1732.5	38 3	2.441	785.2

Molecular weight: **226,58.** Radius of the Capillary tube 0.04242 cm.; in the observations indicated by *, it was: 0.04583 cm. Depth: 0.1 mm.

The beautifully crystallised compound melts at 73°.2 C.; under a pressure of 20 mm. it boils at 111° C.

The specific gravity can be calculated (KOPP) from the equation: $d_{4°} = 2.6712 - 0\,002166\ (t - 75°) - 0\,00000072\ (t - 75°)^2$.

The temperature-coefficient of γ is fairly constant and about **1,66** Erg per degree.

8.

Bismuthchloride: $BiCl_3$.

Temperature in ° C	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity $d_{4°}$	Molecular Surface-energy γ in Erg per cm²
	in mm. mercury of 0° C	in Dynes			
271°	2.271	3028.	66.2	3.811	1254.4
304	2 119	2825	61.8	3.735	1187.0
331	1.994	2658	58.1	3 682	1126.6
353	1 896	2528	55.3	3.621	1084.3
382	1.782	2376	52.0	3.554	1032.4

Molecular weight: **314.38.** Radius of the Capillary tube 0.04363 cm. At 18° C. Depth 0.1 mm.

The salt, which melts at 230° C., was purified by distillation in a stream of dry hydrochloric acid. Above 400° C. no reliable measurements were possible, because of the attacking of the platinum capillary tube by the vapours. The measurements can only be considered as approximative ones, because of the partial decomposition of the $BiCl_3$ by the air, which cannot be avoided under these circumstances. The specific weight at 254° C. was: 3.851; at 281° C. 3 789; at 304° C. 3 735. At t° C it is $d_{4°} = 3\,860 - 0.00232\ (t - 250°)$. The temperature-coefficient of γ is between 271° and 831° C about **2.14** Erg; between 331° and 353° C.: about **1.92** Erg; and between 353° and 382° C. **1.78** Erg. per degree Celsius.

9.

Bismuthbromide: $BiBr_3$.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg per cm².	Specific gravity d_{4°	Molecular Surface-energy γ in Erg per cm
	in mm. mercury of 0° C	in Dynes			
250°	2.272	3029	66 5	4.598	1407.6
281	2.172	2893	63.6	4.525	1360.6
299	2.103	2804	61.6	4.471	1328.5
320	2.032	2709	59.5	4.416	1293.8
346	1.936	2581	56.7	4.348	1245.7
370	1.836	2448	53.8	4.286	1191.3
389	1.774	2366	52.0	4.237	1162.3
417	1.668	2224	48.9	4.164	1105.8
442	1.575	2100	46.2	4.099	1055.8

Molecular weight: **447,76.**

Radius of the Capillary tube: 0.04381 cm. at 150 C.

Depth: 0.1 mm.

The salt was prepared from the purest bismuth and bromine, and purified by distillation; it melts at about 250° C. into a yellow liquid, becoming darker at higher temperatures At 271°.5 C. the density was: 4.572; at 301° C. 4.466; at 330° C.: 4.390. At t° C. it is generally: $d_{4^\circ} = 4.598 - 0.0026\,(t = 250°)$

The temperature-coefficient of γ increases slowly from **1,76** Erg between 250° and 389°, to about **2,0** Erg per degree at higher temperatures.

§ **3.** If now we review the results obtained, on comparison we can derive from them the following conclusions (vid. fig. 1).

Name of the Substance:	Temperature-coefficient of γ:
Sulphurmonochloride	2.24 to 1.79
Phosphorustrichloride	1.61
Phosphorustribromide	0.81 to 2.63
Arsenictrichloride	1.40
Arsenictribromide	2.05 to 0.98
Antimonytrichloride	1.66
Bismuthumtrichloride	2.14 to 1.78
Bismuthumtribromide	1.76 to 2.0

Although the values of $\frac{\partial \mu}{\partial t}$ are not great, and generally *smaller* than the normal value of **2.24** Erg per degree, they are however in all cases appreciably greater than such as occurred in the case of the inorganic molten salts; these values here point in every respect to close analogy with the behaviour of organic liquids.

Fig. 1.

Doubtless the influence of the much lower boiling- and melting-temperatures, which are typical for these substances in comparison with the salts mentioned, makes itself felt here.

As for the mutual situation of the χ-t-curves (fig. 1), this appears to be quite regular, just as in the case of the alcali-halogenides, but just *in the reverse direction, because at the same temperature, χ appears to increase with the atomic weight of the element combined with the halogen.* A comparison of the χ t-curves of PCl_3, $AsCl_3$, $SbCl_3$ and $BiCl_3$ on one side, and of PBr_3, $AsBr_3$ and $BiBr_3$ on the other side, shows this immediately. It is remarkable however, that the same is the case here for the halogens: if the χ-t-curves of PCl_3, PBr_3 and PI_3 are compared with each other, and also those of $AsCl_3$ and $AsBr_3$, and of $BiCl_3$ and $BiBr_3$, — it appears, that *at the same temperatures the values of χ are the greater, as the atomic weight of the halogen increases;* i.e. just in the reverse direction as formerly was found in the case of the halogenides of the alcali-metals [1]). It is very probable that the cause of this striking deviation must be attributed to the much less pronounced contrast in electrochemical character, which the metalloids *P*, *As* and *Sb* show in comparison with the *halogens*, in comparison with that of the strongly electropositive *alcali-metals* against those same halogens,

[1]) F. M. JAEGER. These Proceedings **17**, 568, 570. (1914).

and the degree of dissociation α (no doubt influenced by it) of the molten alcali-halogenides on one side, and the *P*, *As* and *Sb*-halogenides on the other side.

In the case of the *Bi*-salts, which approach already much more closely to the real metallic salts, the influence of the combined halogen manifests itself immediately in another way: the χ-*t*-curve for $BiBr_3$, although for a greater part coinciding with that of $BiCl_3$, is situated just *beneath* the latter. Previously we found in the case of organic liquids, being also compounds, which do not show an electrolytical dissociation, that the presence of electronegative atom-groups or elements tends generally to increase the values of χ. The specific influence of the substitution of three chlorine-atoms by three bromine-atoms, or of *As* by *Sb*, etc. in the case of these also only slightly associated liquids, perhaps could be thought comparable with the mentioned peculiarity.

For the μ-*t*-curves the same regularities as for χ-*t*-curves, are present in this case; contrary to what was found in the series of the alcali-salts also here the μ-*t*-curves are situated regularly above or beneath each other, all in connection with the atomic weight of the combined elements. The curve for $BiCl_3$ is here certainly situated completely *beneath* that for $BiBr_3$, while those for $AsBr_3$ and $SbCl_3$ are almost coinciding. (fig.) 2).

Thus contrary to these of the alcali-halogenides, the μ-*t*-curves

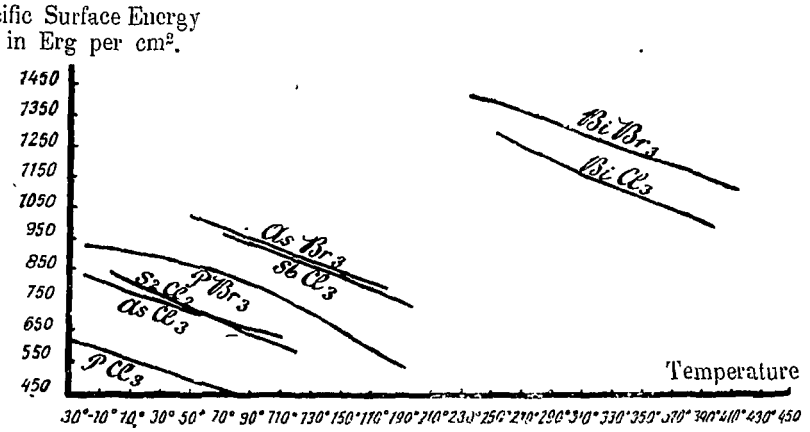

Fig. 2.

are here situated in the *same* arrangement as the χ-*t*-curves; an irregularity like that found in the first case, is not observed here, which evidently is connected with the fact, that no appreciable electrolytic dissociation plays a rôle here.

Laboratory for Inorganic and Physical Chemistry of the University.
Groningen, Holland, June 1916.