to the adopted masses also cannot help us. If the mass of Mercury were multiplied by 3, which of course in itself is outside all limits of probability, the node of Venus would be put right, but we should then have a still larger discrepancy e.g. in the perihelion of Venus. It is not possible to find a system of masses which will reduce all residuals to within their mean errors.

Chemistry. — *"Investigations on the Temperature-Coefficient of the Free Molecular Surface-Energy, of Liquids between* — 80° *and* 1650° *C."* · **XV**. *"The Determination of the Specific Gravity of molten Salts, and of the Temperature-Coefficient of their Molecular-Surface-Energy"*. By Prof. Dr. F. M. JAEGER and Dr. JUL. KAHN.

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

§ 1. For the calculation of the molecular free surface-energy of the molten salts and other compounds, about which we have previously communicated [1]), it is necessary to know the specific gravity of the investigated liquids at temperatures ranging from — 80° up to 1650° C.

As far as organic liquids are concerned, the usual and generally known methods can be applied, — at least if the temperatures of measurement are-not too far apart from the range usually considered in laboratory-experiments. In those cases we used in the first place the *pycnometer.* Commonly this consisted in a double-walled vessel, the space between the glass-walls being carefully evacuated; it was closed by means of a ground thermometer. In most cases the densities were determined in thermostats at 25°, 50° and 75° C. In the work with liquids of low boilingpoint such measurements had to be made also at the temperature of melting ice, or in refrigerant mixtures of salt and ice, or in those of solid carbondioxide and alcool; in these cases the pycnometer is evidently not a suitable instrument, and the pycnometrical method appears for many reasons much less adapted than the *volumetrical* method.

More particularly in the determination of the specific gravities of the low-boiling aliphatic *amines*, which moreover will absorb readily the carbondioxide and the water-vapour from the atmosphere, the *volumeter* appeared to be the only applicable instrument, while

ecliptic. For the planetary precession we should have a correction amounting to +0."30 per century. These residuals are not appreciably better than those given above in the text. (Note added in the English translation).

[1]) F. M. JAEGER and Collaborators, these Proceedings, 1914, '15 and '16.

furthermore special precautions had to be taken in filling the apparatus. Therefore the filling of the instrument was executed in the following way: The volatile liquid is contained in a sealed vessel A (fig. 1), which is placed in a DEWAR-glass, in a mixture of solid carbondioxide and alcool. On continuous cooling the vessel is rapidly sealed to the further glass-apparatus, after the capillary glass-tube is broken off. While the fat-free stopcocks r_1 and r_2 are closed, a current of dry air, freed from water and carbondioxide by means of quick lime and sodium hydroxide, is introduced by T_1. Then the tube T_1 is sealed off, and now the volumeter is sealed to the appa-
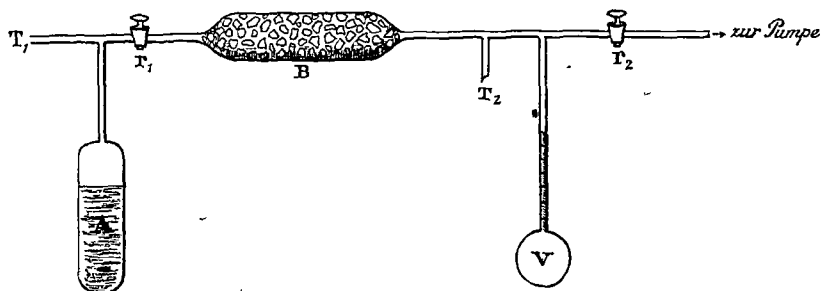

Fig. 1.

ratus, during which operation the air can escape through T_2. This being finished, also T_2 is sealed off; then the stopcocks r_1 and r_2 are opened, and the whole apparatus is evacuated. Now the volumeter is placed into the cold bath, and the stopcock r_1 is opened again; after the desired quantity of liquid is distilled from A into V, during which the vapour in passing again the tube B filled with dry and pure BaO, gives off its last traces of humidity, the stem of V is sealed-off at a point lying considerably higher than the highest division of the capillary tube.

Then the whole apparatus is accurately weighed. Now the volumetrical measurements are made at the desired temperatures; and finally the volumeter is carefully opened by removing the end of the capillary tube, and after cleaning and completely drying, the empty apparatus is weighed again, together with the removed piece of glass. The difference of the two weights gives the weight of the liquid used, whose volumina now are determined at different temperatures, because the volumeter has been accurately calibrated previously. After the necessary corrections the specific gravity at the said temperatures can be easily calculated from these data. The capillary tube has to be completely cylindrical, they were thick-walled, and accurately calibrated by means of liquids, whose specific gravities at a whole series of temperatures were exactly known.

Experience shows, that in most cases the third figure could still be considered to be certain, — which accuracy is wholly sufficient for our purpose.

2. Of course neither a pycnometer nor a volumeter could be used in cases, where the organic substances had a too high melting-point; and à fortiori this was the case with the inorganic salts melting at extremely high temperatures. In these cases the only way was to use a *hydrostatical* method, in which a sinker is used, which is described in detail further-on. Only in such cases, where the substance investigated appeared to be so volatile, as to give a rapid sublimation against the colder parts of the suspension-wire, it was not possible to apply this method. In such, — happily only rare cases, — the determination of the specific weight must be given up completely; the same was the case, if the viscosity of the molten mass or its surface-energy surpassed certain limits.

The apparatus used in the determinations of the specific gravities of such molten salts, up to temperatures of 1500° C, had finally, after many alterations and varied constructions, the here described form (fig. 2).

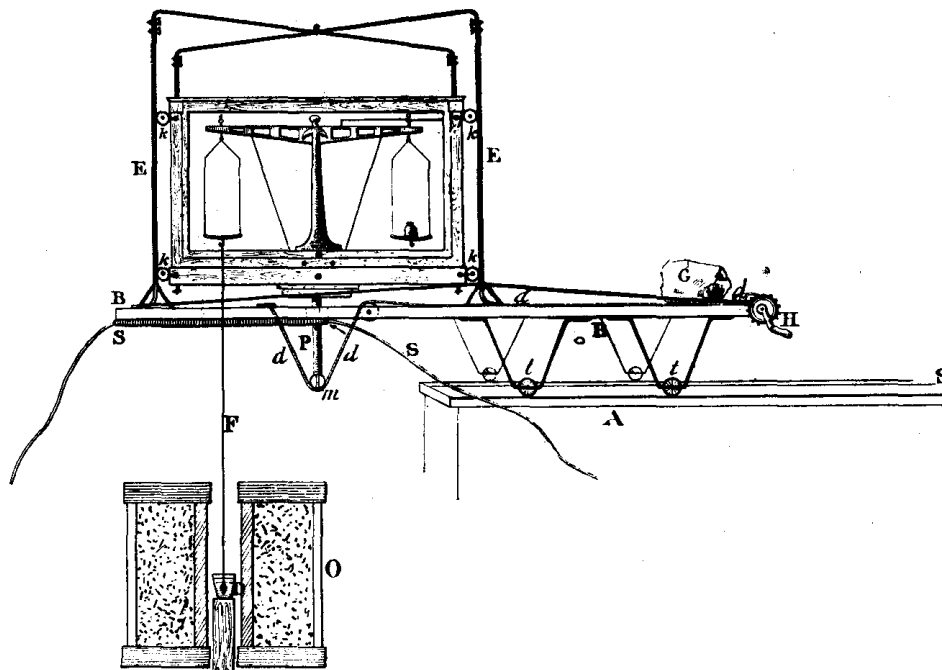To one of the scales of a sensitive analytical balance a platinum-

Fig. 2.

wire as thin as possible, *F* (about 80 cm. long) was fixed by means of a small ringlet. For measurements from 1200° to 1600° C., this wire has to be at least 0.3 mm. thick, because it would break

otherwise too easily, the platinum being very soft at such high tem-
peratures. The wire passes through a narrow, cylindrical hole in
the bottom of the balance-case, a second hole of the same shape
in the board *B*, and a third small canal in the water-screen *S*,
which is continuously passed by a stream of cold water, so as to
prevent the heat-radiation from the furnace to the balance-case. At
its free end the wire bears a massive platinum double-conus *D*,
made from iridium-free platinum; this-sinker had in our experiments
a weight' of about 12,1 grams. The balance could move up-and-
down by means of four brass pulleys *k*, gliding along the four iron
bars *E*; it is supported by a movable pillar *P*, to which at one
side also a pulley *m* is fixed, resting on a thin steel cable *d*. By
means of a windlass and handle *H* this cable can be shortened or
lengthened, the balance being thus moved upwards or downwards.
The board *B*, can be rolled to and fro by the wheels *t*, moving
on the iron rails fixed on *A*; in this way the balance can be placed
above the furnace *O*, or, if necessary, it can be removed from it.
G furthermore is a heavy iron weight, which serves for the equili-
brium and stability of the whole apparatus, which in the neigh-
bourhood of the furnace is firmly fixed upon a heavy table.

- Now the platinum sinker with wire is weighed in air; then the
balance is dropped till the conus is dipped into the liquid, until the
-surface of this comes to a fix-point on the wire. The temperature
of the liquid is determined by means of a thermoelement placed in
it quite near to the sinker, by measuring its electromotive force with
the potentiometer-arrangement - always used in this laboratory [1]). By
measuring the force, with which the sinker is driven upwards, if
the balance can swing freely, the specific weight of the liquid can
be calculated, and all necessary corrections can be taken into account.

The described method was previously tried by means of a number
of organic liquids of known density. The result was, that the thus
obtained data agreed completely with those obtained by means of
the pycnometer, as far as the dependence of the density on the
temperature is concerned, moreover also the absolute values appeared
to be the same in both cases. if only a correction was taken into
account for the capillary influence of the liquid on the wire, which
c.p. appeared to be directly proportional to the specific surface-
energy χ of the liquid at every temperature. In the case of the
wire used by us this correction appeared to be only slightly more
than about 0.0001 gram per Erg. This amount must be added

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[1]) F. M. JAEGER Eine Anleitung zur Ausführung exakter physiko chemischer
Messungen bei höheren Temperaturen. Groningen, 1913, p. 16—19.

afterwards to the value found for the force, which drives the sinker upwards. Also in the case of the molten salts KNO_3, $NaNO_3$, $LiNO_3$, etc. the _absolute_ values for d_4^0 appeared to agree with those of Goodwin and Mailey [1], if only the observed hydrostatic force was augmented with 0.0001 χ; the temperature-coefficient of d_4^0 moreover appeared to be independent of this correction too. However, the dates obtained in this way, and especially those at extreme temperatures, can only be considered quite exact in two decimals, and the accuracy never surpasses three or four units of the third decimal. For the proposed purpose this degree of accuracy is sufficient; but, moreover, it may be asked if it is possible at all to obtain more accurate data at such extreme temperatures in some other way? Circumstances are rather unfavourable in these measurements; for an increase of the upwards driving force by the choice of a sinker of greater volume, as Goodwin and Mailey did (loco cit), can hardly be considered a real improvement, because the condition of an everywhere equal and homogeneously distributed temperature can only be fulfilled by a volume (as small as possible) of the molten mass and of the whole apparatus in the furnace. Only then the furnace can be used as a real thermostat at very high temperatures [2]. Platinum is, moreover at such high temperatures the only fit material to use; but because of its very high specific weight, the volume of an even very heavy sinker will be only relatively small, and consequently also the observed upwards driving force. There are a number of other disturbing circumstances, e.g. the rather strong damping of the swinging balance, if liquids of appreciable viscosity or surface-tension are investigated; in such cases it is absolutely necessary to keep the liquid at the same temperature for a longer time, if one wishes to be certain of established equilibrium, which must moreover be checked in several ways. All such circumstances diminish the degree of accuracy more or less, so that one may finally be glad to reach the degree of agreement of repeated determinations here mentioned. Especially will this be the case, as most of these molten salts appear to decompose gradually more or less at very high temperatures by, or without, the water-vapour of the atmosphere; their chemical composition being thus altered at the same rate.

Another difficulty again presented itself in measurements of this kind, which is caused by the fact, that most substances possess

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[1] Goodwin and Mailey, Physical Review, **25** 469. (1907); **26**. 28. (1908).

[2] F. M. Jaeger, Eine Anleitung zur Ausführung exakter physiko-chemischer Messungen, u. s. w. Seite 57, 59, u s. w.

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already a considerable vapour-tension at such high temperatures. The evaporated salt sublimes against the colder parts of the suspension wire in the form of very small crystals, or as a thin coherent layer; the increase of weight, corresponding with it, makes .the upwards-driving force also seem smaller than it really is. It is rather· difficult to determine afterwards-the correction necessary by it, or even to estimate its magnitude with any certainty.

Although the thus obtained results cannot be considered so accurate as possibly we should wish, we think it, however, wholly justified to consider them as giving a very ·satisfactory idea of the true specific gravity of this liquids, and to give a sufficiently accurate result for the dependence of the specific gravity on the temperature in the case of these molten salts.

The weight of the platinum conus with the submerged part of the wire, was at 25° C 12,1772 grams (corr.), the specific weight of the platinum at 25° C. was pycnometrically determined at 21,47, and at 0° C. at 21,485. At $t°$ C. it was calculated from the expression.

$$d_{4°}^{Pt} \frac{21,485}{1 + 3(0,000008868\, t + 0,000000001324\, t')}.$$

Let P be the weight of the sinker with wire in air, p its weight if submerged in the liquid, then $P—p$ is the upwards driving force, as it *seems* to -be. The real force A however is greater, and equal to : $P—p + 0,0001\, \chi_t$.

From this it follows:

$$\frac{A}{P} = \frac{\text{specific weight of the liquid — specific weight of air}}{\text{specific weight of the platinum}},$$

from which thus the specific weight of the liquid at $t°$ C. follows to be:

$$d_{4°}^t = \frac{A \cdot d_t^{Pt}}{12,1772} + 0,001.$$

For all salts the specific gravities were calculated in this way.

§ 3. In the following pages we have shortly reviewed the data thus obtained in the case of a series of salts and other inorganic compounds. Of every salt we have reproduced the figures for three temperatures at least, and we have, moreover, mentioned the general empirical formula, from which the density at other temperatures were intra or extrapolated. We have added the values of the molecular free surface-energies of the liquids at the same temperatures, in Erg per c m², and some remarks on the magnitude of its temperature-

coefficient $\frac{\partial \mu}{\partial t}$. Finally the complete measurements of three inorganic salts not yet previously [1]) described, are reproduced here too.

LiF

t°:	d_{4°:	ν in Erg :
887°	1.780	1484.5
973	1.740	1452.1
1058	1.699	1421.3

$d_{4^\circ}^{t} = 1.798 - 0.0004375 \ (t - 850)$.

The temperature-coefficient $\frac{\partial \mu}{\partial t}$ increases from about **0,40** Erg per degree between 900° and 1050° to about **0,58** Erg between 1050° and 1200° C.

LiCl.

t°:	d_{4°:	ν in Erg:
626°	1.490	1274.8
683	1.465	1262.0
732	1.444	1256.5

$d_{4^\circ}^{t^\circ} = 1.501 - 0.000432 \ (t - 600)$.

$\frac{\partial \mu}{\partial t}$ has a mean value of about **0,47** Eig per degree.

Li₂SO₄.

t°:	d_{4°:	ν in Erg:
908°	1.984	3213.5
1005	1.945	3159
1112	1.901	3100

$d_{4^\circ}^{t^\circ} = 2.008 - 0.000407 \ (t - 850)$.

$\frac{\partial \mu}{\partial t}$ has a mean value of **0,50** Erg per degree.

LiNO₃.

t°.	d_{4°:	ν in Erg:
288°	1.762	1336
341	1.732	1311.2
454	1.770	1260.2
546	1.621	1212.8

$d_{4^\circ}^{t} = 1.755 - 0.000546 \ (t - 300)$.

$\frac{\partial \mu}{\partial t}$ has a mean value of **0,45** Erg per degree.

NaF

t°:	d_{4°:	ν in Erg.
1017°	1.932	1548.3
1119	1.875	1501.9
1214	1.821	1445.1

$d_{4^\circ}^{t^\circ} - 1.942 - 0.000564 \ (t - 1000)$.

$\frac{\partial \mu}{\partial t}$ is rather constant, and has a mean value of **0,52** Erg per degree.

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[1]) F. M. JAEGER, these Pioccedjngs **17**, 555 and 571, (1914).

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NaCl.

t^o:	d_4^o	μ in Erg:
823°	1.535	1276.5
854	1.516	1259.1
885	1 496	1244 4

$$d_{4^o}^{t^o} = 1\,549 - 0.0000626\ (t - 800).$$

$\dfrac{\partial \mu}{\partial t}$ has a mean value of about **0.48** Erg per degree.

NaBr.

t^o.	d_4o:	μ in Erg
787°	2 300	1311.9
829	2.269	1293 0
8 80	2 226	1253 4

$$d_{4^o}^t = 2.306 - 0\,00072\ (t - 780) - 0.0000008\ (t - 780)^2.$$

$\dfrac{\partial \mu}{\partial t}$ has a mean value of **0.53** Erg per degree.

NaI.

t^o·	d_4o:	μ in Erg·
675°	2.725	1257
699	2.699	1250
724	2 673	1242

$$d_{4^o}^t = 2.698 - 0.001061\ (t - 700).$$

$\dfrac{\partial \mu}{\partial t}$ increases from 0,29 Erg at 750° C, to a mean value of **0,63** Erg between 815° and 860° C.

Na₂SO₄.

t^o:	d_4o:	μ in Erg:
926°	2.049	3240
988	2.021	3210
1046	1.991	3203

$$d_{4^o}^{t^o} = 2\,061 - 0\,000483\,(t - 900).$$

$\dfrac{\partial \mu}{\partial t}$ can be estimated at about **0,30** Erg per degree.

Na₂MoO₄.

t^o	d_4o·	μ in Erg.
804°	2.730	3636
931	2.648	3512
1063	2.567	3388

$$d_{4^o}^{t^o} = 2.795 - 0.000629\ (t - 700).$$

Between 700° and 800° $\dfrac{\partial \mu}{\partial t}$ is **1,2** Erg per degree, between 800° and 1035° C. it is **0,98** Erg; and between 1035° and 1171° C. it is **0,56** Erg per degree.

Na₂WoO₄.

t^o:	d_4o·	μ in Erg
917°	3.685	3531
1128	3.502	3353
1330	3.356	3168

$$d_{4^o}^{t^o} = 3,673 - 0\,0009275\,(t - 930) + 0.000000337\,(t - 930)^2.$$

Between 700° and 1000° $\dfrac{\partial \mu}{\partial t}$ is about **0,64** Erg per degree; between 1515° and 1600° C. it is about **0,98** Erg.

NaNO$_3$

t^o	d_{4^o}	μ in Erg
350°	1 880	1502
400	1.847	1486
450	1 813	1464
500	1.780	1442
550	1.746	1418

$$d_{4^o}^{t^o} = 1.914 - 0\ 000672\ (t - 300).$$

Between 320° and 360° $\dfrac{d\mu}{\partial t}$ is **0,24** Erg, between 350° and 425° C : **0,34** Erg , between 425° and 600° : **0,45** Erg per degree.

NaPO$_3$.

t^o:	d_{4^o}:	μ in Erg:
905°	2.147	2532
1007	2.102	2490

$$d_{4^o}^{t^o} = 2.193 - 0.00044\ (t - 800)$$

$\dfrac{\partial \mu}{\partial t}$ is up to 1200° about **0,43** Erg, to 1270° C. **0,61** Erg, and at 1500° C. about **1,1** Erg per degree.

KF.

t^o	d_{4^o}	μ in Erg
913°	1 869	1368
986	1.819	1342
1054	1.775	1310

$$d_{4^o}^{t^o} = 1.878 - 0.000669\ (t - 900).$$

Between 900° and 960° $\dfrac{\partial \mu}{\partial t}$ **0,33** Erg; between 960° and 1060°: **0,45** Erg, and it increases gradually to **0,83** Erg between 1275° and 1310° C

KCl.

t^o:	d_{4^o}:	μ in Erg
785°	1.517	1299 0
837	1.485	1269 3
878	1.461 ·	1241.0

$$d_{4^o}^{t} = 1.539 - 0.0005947\ (t - 750).$$

$\dfrac{\partial \mu}{\partial t}$ is constant, and **0,68** Erg per degree.

KBr.

t^o:	a_{4^o}	ν in Erg .
751°	2 105	1286
776	2.085	1270
802	2.064	1246

$$d_{4^o}^{t^o} = 2\ 106 - 0.000799\ (t - 750)$$

$\dfrac{\partial \mu}{\partial t}$ has a mean value of **0,76** Erg per degree.

KI.

t^o ·	d_{4^o} ·	μ in Erg ·
700°	2 431	1329
725	2.405	1288
751	2.378	1247

$$d_{4^o}^{t^o} = 2.431 - 0.001022\ (t - 700).$$

Between 730° and 765° $\dfrac{\partial \mu}{\partial t}$ is **1,58** Erg; between 765° and 815° C. : **0,67** Erg, and at higher temperatures **0,41** Erg per degree.

K_2SO_4.

$t°$	d_4^o	μ in Erg
1102°	1.871	2931
1202	1.815	2861
1291	1.768	2770

$d_4^{t^o} = 1.872 - 0.000545\,(t - 1100)$.

$\dfrac{\partial \mu}{\partial t}$ has a mean value of 0,90 Erg per degree Celsius.

$K_2Cr_2O_7$.

$t°$	d_4^o	μ in Erg
420°	2.271	3620
463	2.242	3586
497	2.217	3575

$d_4^{t^o} = 2.285 - 0.000695\,(t - 400)$.

Between 480° and 540° C. $\dfrac{\partial \mu}{\partial t}$ can be estimated to be 0,86 Erg per degree.

K_2MoO_4.

$t°$	d_4^o	μ in Erg
964°	2.342	3227
1124	2.243	3128
1324	2.110	2933

$d_4^{t^o} = 2\,342 - 0.00060\,(t - 964) - 0.000000128\,(t - 964)^2$.

$\dfrac{\partial \mu}{\partial t}$ has a mean value of 0,79 Erg per degree.

K_2WO_4.

$t°$	d_4^o	μ in Erg
991°	3.120	3376
1201	2.954	3051
1361	2.837	2806

$d_4^{t^o} = 3.113 - 0.00082\,(t - 1000) + 0.000000162\,(t - 1000)^2$.

$\dfrac{\partial \mu}{\partial t}$ has a mean value of 1,6 Erg per degree.

KNO_3.

$t°$	d_4^o	μ in Erg
394°	1.826	1588
460	1.774	1538
532	1.720	1478

$d_4^{t^o} = 1.898 - 0.0007681\,(t - 300°)$*).

$\dfrac{\partial \mu}{\partial t}$ has a mean value of 0,83 Erg per degree

KPO_3

$t°$	d_4^o	μ in Erg
988°	2.030	2244
1090	1.986	2172
1195	1.941	2074

$d_4^t = 2\,111 - 0.00043\,(t - 800)$.

Up to 1200° C. $\dfrac{\partial \mu}{\partial t}$ is constant, and 0,91 Erg per degree; afterwards it increases to about 1,28 Erg per degree.

*) In the Dutch paper this formula contains an error; the numbers given here are the right ones

RbF.

t°:	d_{4°	μ in Erg
820°	2.878	1371
914	2.785	1287
1006	2.690	1230

$$d_{4^\circ}^{t^\circ} = 2\,873 - 0\,000967\,(t - 825) - 0.000000247\,(t - 825)^2.$$

Between 802° and 887° $\frac{\partial\mu}{\partial t}$ is about **1,0** Erg per degree, between 887° and 1037° C. **0,56** Erg, and afterwards· **0,40** Erg per degree.

RbCl.

t°	d_{4°	μ in Erg.
734°	2.101	1449
786	2 059	1400
822	2 029	1366

$$d_{4^\circ}^{t^\circ} = 2.129 - 0\,000823\,(t - 700)$$

$\frac{\partial\mu}{\partial t}$ is rather constant, and has a mean value of **1,02** Erg per degree.

RbBr

t°:	d_{4°	μ in Erg
697°	2 691	1401
715	2.672	1389
744	2.640	1366
780	2 600	1339

$$d_{4^\circ}^{t^\circ} = 2.688 - 0\,001096\,(t - 700)$$

$\frac{\partial\mu}{\partial t}$ is rather constant, and **0,77** Erg per degree.

RbJ.

t°:	d_{4°	μ in Erg.
700°	2.798	1389
750	2 742	1338
800	2.687	1288

$$d_{4^\circ}^{t^\circ} = 2\,798 - 0.001107\,(t - 700).$$

$\frac{\partial\mu}{\partial t}$ is rather constant, and equal to **0,95** Erg per degree.

Rb₂SO₄.

t°:	d_{4°	μ in Erg:
1101°	2 528	2923
1204	2.458	2813
1307	2.391	2735

$$d_{4^\circ}^{t^\circ} = 2.562 - 0\,000665\,(t - 1050).$$

Between 1086° and 1112° C $\frac{\partial\mu}{\partial t}$ is **1,98** Erg; between 1112° and 1145°: **1,12** Erg; between 1145° and 1234° C.· **0,93** Erg; to 1350° C. **0,72** Erg, to 1334° C. **0,45** Erg; and up to 1550° C.· **0,27** Erg per degree Celsius.

RbNO₃

t°:	d_{4°	μ in Erg
348°	2.446	1626
445	2.350	1555
555	2.245	1470

$$d_{4^\circ}^{t^\circ} = 2.492 - 0.000972\,(t - 300).$$

$\frac{\partial\mu}{\partial t}$ has a rather constant mean value of **0,78** Erg per degree.

CsF.

t°:	d_{40}.	ν in Erg.
720°	3.586	1271
771	3 522	1239
824	3 457	1200

$$d_{40}^{t^\circ} = 3.611 - 0\,001234\,(t - 700).$$

Originally $\dfrac{\partial \mu}{\partial t}$ is **0,72** Erg per degree, above 930° C. however it diminishes with increasing temperature to **0,36** Erg at 1100° C.

CsCl.

t°:	d_{40}:	ν in Erg
660°	2 775	1380
701	2.731	1358
741	2.688	1278

$$d_{40}^{t^\circ} = 2.786 - 0.00108\,(t - 650).$$

Up to 980° $\dfrac{\partial \mu}{\partial t}$ is about **0,80** Erg per degree, afterwards it increases rapidly **1,17** Erg to 1035° C ; and **1,70** Erg to 1080° C

CsBr.

t°:	d_{40}·	ν in Erg
662°	3 109	1362
702	3.054	1325
742	3.001	1278

$$d_{40}^{t^\circ} = 3.125 - 0.00134\,(t - 650)$$

Between 660° and 700° $\dfrac{\partial \mu}{\partial t}$ is **0,90** Erg per degree, it then diminishes gradually to about **0,57** Erg between 860° and 970° C.

CsJ.

t°:,	d_{40}:	ν in Erg:
639°	3.176	1394
670	3.138	1369
701	3 101	1330

$$d_{40}^{t^\circ} = 3.175 - 0.001222\,(t - 640).$$

$\dfrac{\partial \mu}{\partial t}$ has a rather constant mean value of **0,82** Erg per degree.

Cs$_2$SO$_4$.

t°:	d_{40}	ν in Erg
1040°	3.034	2687
1128	2 968	2546
1220	2.890	2435

$$d_{40}^{t^\circ} = 3.034 - 0.000711\,(t - 1040) - 0\,000000494)(t - 1040)^2.$$

Between 1036° and 1100° C. is $\dfrac{\partial \mu}{\partial t}$ about **1,91** Erg, between 1100° and 1220° C.· **1,16** Erg, between 1220° and 1425° C. **0,70** Erg, and up to 1530° C · about **0,43** Erg per degree.

CsNO$_3$.

t°:	d_{40}·	ν in Erg:
445°	2.774	1532
481	2.733	1484
529	2 680	1431
575	2 699	1399

$$d_{40}^{t^\circ} = 2.824 - 0.001114\,(t - 400).$$

To 600° C. $\dfrac{\partial \mu}{\partial t}$ has a mean value of **1,18** Erg per degree; afterwards it decreases rapidly to about: **0,42** Erg.

Potassiumbichromate: $K_2Cr_2O_7$					
Temperature in ° C	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity d_{4^0}	Molecular Surface-energy μ in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			
420°	4.853	6470	140.1	2 271	—
454	4.825	6433	139.4	2.248	3593
480	4.792	6389	138.4	2.229	3588
504	4 743	6323	137.0	2 213	3568
535	4.672	6229	135.0	2.191	3540

Molecular weight: **294,2.** Radius of the Capillary tube: 0 04315 cm. at 18° C. Depth: 0.1 mm

Above 540°. C. a decomposition sets in, while gas is developed. After corrections the specific gravity at 240° C. is· 2.271; at 462°.7 C.: 2 242; at 497° 4 C.. 2.217. Generally at $t°$ C.: $d_{4^0} = 2.285—0.000695 (t—400)$.

The tempereture-coefficient of γ has a mean value of about **0.86** Erg per degree, at least between 480° and 535° C.

Thallous Nitrate: $TlNO_3$.					
Temperature in ° C.	Maximum Pressure H		Surface-tension γ in Erg per cm².	Specific gravity d_{4^0}	Molecular Surface-energy μ in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			
210°	4.071	5428	117.3	4.899	1681.9
245	3.996	5328	115.2	4.838	1665.7
263.5	3.946	5261	113.8	4.806	1652.8
285	3.884	5178	112.0	4.768	1635.2
312	3.806	5075	109.8	4.721	1613.8
339	3.723	4963	107.4	4.674	1589.0
364	3 645	4860	105.2	4.630	1566.4
389	3.562	4754	102.8	4 586	1540.4
430	3.445	4592	99.5	4.515	1506.5

Molecular weight: **266.01.** Radius of the Capillary tube: 0.04315 cm. at 15° C. Depth: 0.1 mm.

The salt melts at 206° C. to a clear colourless liquid. The specific gravity at 214° C. was: 4.892; at 254° C.: 4.824; at 290° C : 4.74. At $t°$ C.: $d_{4^0} = 4.917—0.00175 (t-200)$.

The temperature-coefficient of γ is about **0 81** Erg per degree, as a mean value.

Temperature in ° C.	Maximum Pressure H		Surface-tension χ in Erg per cm².	Specific gravity d_{40}	Molecular Surface-energy μ in Erg per cm².
	in mm. mercury of 0° C.	in Dynes			

<table>
<tr><td colspan="6" align="center">Stannous Chloride: <i>SnCl₂</i>.</td></tr>
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307°	3.331	4447	97.0	3.289	1449
328	3.298	4397	96.2	3.263	1445
361	3.216	4283	93.9	3.222	1422
377	3.155	4207	92.0	3.202	1402
405	3.048	4064	89.0	3.166	1364
430	2.963	3951	86.4	3.135	1333
452	2.874	3832	83.9	3.108	1302
480	2.796	3728	81.6	3.072	1277

Molecular weight: **189.92**. Radius of the Capillary tube: 0.04363 cm. at 18° C. Depth: 0.1 mm.

The substance was purified by distillation in a stream of dry hydrochloric acid. The salt melts at 250° C. At 290° C. the specific gravity is: 3.310; at 345° C.: 3.241; at 398°.7 C.: 3.174. In general at t° C.: $d_{40} = 3.298 - 0.001253$ ($t-300$). The temperature-coefficient of μ has a mean value of about **1.0** Erg per degree.

§ 5. If now we review once more the results obtained in the case of these molten salts (see the following table), it becomes quite clear, that an evident difference in behaviour in comparison with the organic liquids can be stated with respect to the *very small* values of the temperature-coefficient $\dfrac{\partial\mu}{\partial t}$. While in the case of organic liquids the normal values of $\dfrac{\partial\mu}{\partial t}$ is about **2.24** Erg per degree Celsius, it is commonly *much smaller* in the case of molten salts, and varies there between **0.3** and **1.0** Erg per degree. Although a special regularity in the magnitude of $\dfrac{\partial\mu}{\partial t}$ in the different cases can *not* be stated, the mean value of it in the case of homologous salts of the same halogenide seems to show a tendency to increase generally with augmenting atomic weight of the metal. Formerly it has occasionally been concluded from the very small values of $\dfrac{\partial\mu}{\partial t}$ in the case of molten salts, [1] that these should be *associated* to a rather high degree. If one assumes, that for such electrolytes indeed the same kind of

[1] BOTTOMLEY, Journ. Chem. Soc. **83**, 1424, (1903); a.o.

Metal:	Fluoride:	Chloride:	Bromide:	Iodide:	Sulphate:	Nitrate:	Molybdate:	Trystate:	Metaphosphate:
Lithium	0.40 tot 0.58	0.47	—	—	0.50	0.45	—	—	—
Sodium	0.52	0.48	0.53	0.29 tot 0.63	0.30	0.24 tot 0.45	1.2 tot 0.56	0.64 tot 0.98	0.43 tot 1.1
Potassium	0.33 tot 0.83	0.68	0.76	1.58 tot 0.41	0.90	0.83	0.79	—	0.91 tot 1.28
Rubidium	1.0 tot 0.40	1.02	0.77	0.95	1.98 tot 0.27	0.78	—	—	—
Caesium	0.72 tot 0.36	0.80 tot 1.7	0.90 tot 0.57	0.82	1.91 tot 0.43	1.18 tot 0.42	—	—	—
Thallium	—	—	—	—	—	0.81	—	—	—
Stannum	—	1.0	—	—	—	—	—	—	—

considerations can be used, as for the organic liquids, this conclusion may appear as a direct and justified consequence of theory. But in our opinion this can hardly be true: for all conclusions based upon the rule of Eötvös, premises implicitely the validity of the law of corresponding states. Now it must appear highly improbable, that this law could hold really in the case of electrolytically dissociated substances as molten salts are, where the degree of dissociation, moreover, varies doubtlessly with the temperature. And if the law of corresponding states for such electrolytes is doubted, then at the same time all arguments lose their validity, which must serve to sustain the view, that the values of $\frac{\partial \mu}{\partial t}$ could prove the associated state of such molten salts.

Moreover we wish to draw attention here to a second fact in the case of these compounds. Formerly [1]) the first of us was able to show, that in the case of the homologous molten *halogenides* of the alcali-metals a *regular* shifting of the χ-t-curves with respect to each other, in connection with the atomic weights of the halogens or of the alcali-metals, can be stated.

It occurs in such a direction, that at a same temperature t the value of χ in every series of halogenides diminishes regularly with the increase of the atomic weight, as well of the alcali-metal, as of the halogen (loco cit.). If, however, instead of the mutual situation of the χ-t-curves, that of the μ-t-curves is compared in an analogous way, this regularity appears to have vanished almost totally. Thus e.g. the μ-t-curve for NaF is situated appreciably *higher* than that for LiF, in the case of the *chlorides* the corresponding curve for the Rb-salt is situated much *higher* than for the Na-salt, this one however again *higher* than in the case of the K-salt, while the last curve is *higher* than that for $LiCl$. The precedence in the case of the *bromides*, in a decreasing direction, is: Rb, Na, and K,Cs. — both the last mentioned curves almost completely coinciding. For the *iodides* it is in the same way: Rb, Cs, K, Na. On the other hand, with the arrangement in the case of the Li-salts the μ-t-curve for the *fluoride* appears, — it is true, — *much higher* than that for the *chloride*; but in the case of the Na-salts the precedence is in a decreasing sense; F, Br, Cl, I; in the case of the K-salts in the same way; F, Cl, Br, I; with the Rb-salts: Cl, F, Br, I; and in the case of the Cs-salts: Cl, Br, I, F.

Nowhere, however, can there be stated a regularity, perfect in any respect.

[1]) F. M. JAEGER, these Proceedings, 17, 555, 571, (1914).

If now it is once more remembered that $\mu = \chi \cdot v^{2/3}$, 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 $v = \dfrac{M}{d}$, 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* a 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 $a < 1$. 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.