With this the antiserum and serum were always both inactive, so that we have nothing to do with any possible anaphylatoxin.

If one again injects the mixture in which a precipitate has been formed subconjunctively, one will find a rather strong swelling the next few days, which at a morphological examination again seems to contain polynucleous cells. The controlling animals which had only been injected with serum, were normal again the next day.

If one centrifuges the mixture, the above mentioned liquid is not found to cause a swelling, but the precipitate is. So we have here an analogous conduct as with the corpuscles[1].

I have now tried whether specific albumen precipitations did not show the same conduct, and for this I chose the precipitates of horseserum with colloidal $Fe\,(OH)_3$ and $SiO_2$. Both precipitates gave some swelling and at a morphological investigation polynucleous leucocytosis. This investigation must still be extended.  •

If one injects a prepared animal with specific serum, one gets the same phenomenon: swelling and leucocytosis. This phenomenon is wellknown. I did not yet succeed in proving here as well that the precipitins hold the serum in its place[2], although 1 do think it likely, considering what goes before. For the time being I do not see a chance of preparing a serum which possesses amboceptor against foreign albumen, but no precipitin.

*Amsterdam.*                          *Path. Anat. Laboratory of the University.*

**Chemistry.** — "*The Temperature-coefficients of the free Surface-energy of Liquids at Temperatures from* —80° *to* 1650° *C.* 1. *Methods and Apparatus.* By Prof. Dr. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH).

§ 1. The purpose of the experiments here described was to endeavour to ascertain the relation between the so-called "molecular surface-energy" of molten salts and the temperature, — a relation which has hithertho been studied only in liquids, which possess no electrolytical conductivity.

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[1] The experiments are somewhat analogous to those about the local effect of the anaphylatoxin (FRIEDBERGER), but I always used serum that was made inactive, contrary to the investigators, into the anaphylatoxin.

[2] That is to say subconjunctively. For the cornea other laws probably prevail; there the serum remains in the same place for rather a long time without there being any precipitins (WESSELY, VON SZILY).

A probable relation founded upon the law of corresponding states, between the value of the temperature-coefficient of the expression:

$\chi\left(\dfrac{M}{d}\right)^{2/3}$, and the degree of molecular association of a liquid was first suggested by Eotvos [1]), and later by RAMSAY and SHIELDS[2]) and a number of others[3]). These observations appeared to prove, that the values of these coefficients do not differ much from 2,2 Erg per degree C. for "normal" liquids, while for associated ones they are considerably less. In any event some definite knowledge of the dependence of the free surface-energy $\chi$ upon the temperature will be of high importance for the consideration of all problems, relating to the internal state of liquids.

It can hardly be supposed with any probability, that the law of corresponding states will be found to apply in the case of molten salts, because they are really electrolytes and more or less dissociated. Notwithstanding this, if the investigation should chance to reveal relations in any way analogous to those hitherto supposed to be characteristic of organic liquids, this fact must carefully be considered in estimating the significance of the theoretical speculations mentioned, and especially is this the case, where criteria are sought for judging about the molecular state of liquids in general. In fact, one can better hope to elucidate the influence of chemical constitution on characteristic properties in the case of molten salts, than in the case of the much more complicated organic molecules.

These and other considerations, some years ago (1910) suggested the development[4]) of an experimental method, which should permit the study of the dependence of the molecular surface-energy upon temperature, — even up to temperatures in the vicinity of 1650° C.

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[1]) EOTVOS, Wied. Ann. 27. 448. (1886); VAN DER WAALS, Zeits. f. phys. Chem. 13. 713. (1894). EINSTEIN. Ann. d Phys. 34. 165. (1911.)

[2]) RAMSAY and SHIELDS, Zeits. f. phys. Chemie 12. 433. (1893).

[3]) Vid.: GUYE and collaborators, Journ. de Chim. phys. 5. 81, 97. (1907); 9. 505 (1911); etc.; WALDEN and SWINNE, Zeits. f. phys. Chem. 79, 700. (1912) Bull. Acad. St. Pétersbourg, (1914) 405.

[4]) Preliminary experiments of this kind were begun during my stay at the Geophysical Laboratory in Washington, (U. S. A.), in the winter 1910–1911, and I wish to express my thanks here once more to my friend Dr. A. L. DAY for his kind assistance and most valuable advice in this matter. Through these preliminary experiments the availability of the method up to 1200° C. was clearly established by me, and it became quite clear, in what directions improvements were necessary. The further development was hindered by the building and equipment of the new Chemical Laboratory of the University of Groningen: not earlier, than November 1913 could the first measurements of the present series be made.

With the increase of the temperature of observation, the experimental difficulties of precision-measurements increase very rapidly · measurements, which at room-temperature are of the utmost simplicity, are *often very difficult at 400° C., and commonly almost impossible above 1000° C.* This fact explains, why it has not been possible until now, to communicate the results obtained, because only an extended experience could prove to us the reliability of the method used and the degree of accuracy obtainable.

§ **2.** Of all the methods hithertho described for the determination of surface-tensions, the one most used is the method of measuring the rise of the liquid in capillary tubes. RAMSAY and SHIELDS and most of the investigators who have followed, have used this method. It can however hardly be denied, that the absolute values of $\chi$, obtained by different observers with the same liquids and at the same temperatures, show discrepancies of considerable magnitude. Commonly this lack of agreement is attributed rather to the unequal degree of chemical purity of the materials studied, than to the methods employed. In many of the cases, however the discrepancies were *found with liquids, which can be obtained in a state of complete purity* without extraordinary trouble, so that one is easily inclined to the belief that the method of measuring the capillary column includes some sources of error which are not yet sufficiently known. Possibly adhesion to the walls of the tubes plays a certain role in it, or perhaps the influence of the angle between liquid and solid material may be not completely negligible, as is ordinarily assumed.

However there is a decisive argument against the use of the method of capillary ascension in the following investigations; the walls of the capillary tubes used, were *always* damaged in a greater or less degree by the action of the molten salts. A microscopical examination of the walls of the tubes readily revealed this fact. The method cannot be employed therefore at temperatures, exceeding 400˙ C., because the liquids will always be contaminated and the results will be almost valueless. Furthermore, the method assumes, that a rather long column of liquid can be held throughout its full length at a constant and uniform temperature. At high temperatures this condition can scarcely be fulfilled. The study of large platinum resistance-furnaces has shown convincingly, that even in a central furnace-tube of about 26 c.m. length and 4,5 c.m. diameter, with the heating-coil wound inside, the space of really constant temperature is scarcely

longer than 4 or 5 cm.[1]) Therefore it is absolutely essential in every method intended for exact measurement at high temperatures, that the working-space be reduced to dimensions as small as possible. With respect to the measurements of temperature under such conditions, the available methods will permit making them with an accuracy of $0°,1$ C.,[2]) which is more than sufficient for the purpose. On the other hand, the necessary measurements of the surface-energy must be made in such a way, that the results will have the same degree of accuracy at the highest temperatures, which they possess at lower temperatures, while at the same time the liquid to be studied must be restricted to a space of one or two cubic centimeters.

§ 3. To fulfill these postulations, there is a method which can be used under certain conditions, which was first projected by M. SIMON, and later developed by CANTOR,[3]) while it was successfully used afterwards for researches at lower temperatures by FEUSTEL.[4]) It appeared to be possible to develop the technical procedure in such a way, that the method could be used, without any appreciable loss of accuracy, up to the highest temperatures, which can be measured with the platinum-platinumrhodium thermoelement.

The principle of the method is the measurement of the maximum pressure $H$, prevailing within a very small gas-bubble, which is slowly formed at the circular, knife-edge opening of a capillary tube immersed in the liquid perpendicular to its surface, just at the moment, when the gasbubble is about to burst. The sharp edge of the capillary tube eliminates the influence of the capillary angle. In this way absolute measurements of the surface-energy are possible in Ergs per $cm^2$., if the radius $r$ of the tube, the specific gravity $d$ of the liquid at the temperature of observation, and the depth of immersion $i$ of the tube into the liquid, are known. To obtain the true value of $H$, the readings of the manometer require to be diminished by the hydrostatic pressure, corresponding to this depth of immersion $i$.

The method evidently can only give exact results, if the final state of the gasbubble represents a state of equilibrium, and is thus reached

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[1]) BOTTOMLEY, Journ. of the Chem. Soc. 83. 1421. (1903); LORENZ and KAUFLER, B. d. d. Chem. Ges. 41. 3727. (1908); TRAUBE, ibid. 24. 3074. (1891). Vide also: MOTYLEWSKI, Z. f. anorg. Chem. 38. 410. (1903).

[2]) F. M. JAEGER, Eine Anleitung zur Ausführung exakter physiko-chemischer Messungen bei höheren Temperaturen. (1913). p. 36, 43.

[3]) M. SIMON, Ann. de Chim. et Phys. (3). 32. 5. (1851); CANTOR, Wied. Ann. 47. 399. (1892).

[4]) FEUSTEL, Drude's Ann. 16. 61. (1905); FORCH, ibid. 17. 744. (1905).

passing a series of mere equilibria; that is : the method required to be made practically a *static* one, the final maximum-pressure being independent of the special way, in which the pressure in the growing gas-bubble is gradually augmented.

Thus a *very slow* rise of pressure in the growing gas-bubble is necessary, and only in this way does it appear possible to eliminate the small differences of pressure in the long connecting tubes of the apparatus. For it is well known, that the adjustment of such small pressure-differences takes a considerable time, if the connecting tubes are relatively long.

If the radius of the capillary tube is $r$ (in cm.), the specific gravity of the liquid $d$, and the observed maximum-pressure (in Dynes) is $H$, then the surface-energy $\chi$ (in Erg. pro cm³.) is calculated from CANTOR's expression (loco cit.) :

$$\chi = \frac{rH}{2} - \frac{1}{3}dr^2 - \frac{1}{2}\frac{d^2r^3}{H}.$$

The last two terms of the second member of this equation are usually so small, that they can be neglected in comparison with the experimental errors, as being corrections of the secondary order.

Nevertheless it has become clear, that a special correction requires to be applied to the values calculated in this manner, because of the fact, that in the theoretical deduction of this relation, a simplification is used, which cannot be' considered quite legitimate. We will advert to this correction lateron. (Vid.: VI; under general remarks).

With this limitation extended experience in the use of the method leads to the conviction, that in the form it is used here, one can obtain reliable and, within narrow limits, reproducible results. It has the advantage, that the surface-layer of the liquid is continually renewed, thus the often-observed and troublesome phenomenon of the alteration of this layer, need not be feared. Furthermore one can vary the flowing gas at will with the different liquids, to prevent eventual oxidations or reductions [1]). With these precautions the results can be considered as accurate at 1650° C. as at ordinary temperatures, if only no abnormally high viscosity is encountered in the liquids; for this will destroy to some extent the reliability of the measurements. The influence of the viscosity will be discussed lateron in more detail.

Of all sources of error to be considered : inaccuracy in the

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[1]) As long as the gas is indifferent, i.e. as long as it does not react with the liquid, the results will be quite compaiable, because experience teaches, that the differences in the values of $\chi$, measured with different gases, are vanishingly small in comparison with the experimental errors.

measurements of $r$, of $d_t$, of the pressure $H$, of the reduction-factor of the observed pressure on the manometer to mercury-pressure, of the measurement of temperature, of the depth $i$, etc., — the last mentioned appeared to be the most significant. If all these errors are assumed to be cumulative, the total effect upon the reproducibility of the results, even at $1650°$ C. is still within about $1$ $°/_0$ of the true value of $\chi$, and at lower temperatures about $0.6$ $°/_0$ of that value. With many molten salts, where $H$ is very great and the viscosity very small, the percentage error appeared to be even less than this, not exceeding $0,4°/_0$. For our purpose this degree of accuracy may be considered a very satisfactory one considering the enormous difficulties of measurements at those extreme temperatures. It is also questionable, whether it will be possible to exceed this accuracy at such high temperatures in the near future. And if this could be done, it is very problematical whether much would be gained for the purpose proposed. For experience teaches us, that at those extreme temperatures all compounds are in a state of more or less advanced dissociation, and it can hardly be of any significance to express the surface-energy $\chi$ of such compounds in tenths of Ergs, when the uncertainty in the values of $\chi$, caused by the inevitable admixture of the dissociation-products, will surely be larger than the correction-factors following from this increase in the accuracy of the measurements.

§ 4. In this and the following papers we will successively give an account: (1). Of the experimental arrangements and the manner of procedure, including some instances, illustrating the general adaptability of the method employed in different cases. (2). The results, obtained between $-80°$ and $+270°$ C. in the study of a great number of carboncompounds, in connection with their atomic constitution and the validity of EÖTVÖS' theoretical views. (3). The experiments made to determine the free surface-energy of molten salts, by means of the method here developed. In this connection we will also discuss more in detail the earlier attempts to solve the problem by the method of capillary ascension in glass-tubes. (4). Finally a discussion of the results obtained and a number of considerations of a more general kind will be given, which are suggested by the study and comparison of the data now available.

§ 5. *Apparatus and Experimental Equipment.*
a. In all the measurements pure, dry *nitrogen*, free from oxygen, was used, because even at the highest temperatures this gas appeared

to be quite inert, and to attack neither the compounds studied, nor the thermo-elements. Carbondioxyde can be used as a furnace-atmosphere up to relatively high temperatures, but is often not very suitable, to be bubbled through molten salts under these circumstances, because of its character as an anhydrous acid. Furthermore, at the highest temperatures a slight dissociation is always to be feared. At the same time the dry nitrogen permitted us to drive out the air from the glass bulbs at lower temperatures, and completely prevented the oxidation of the organic liquids studied.
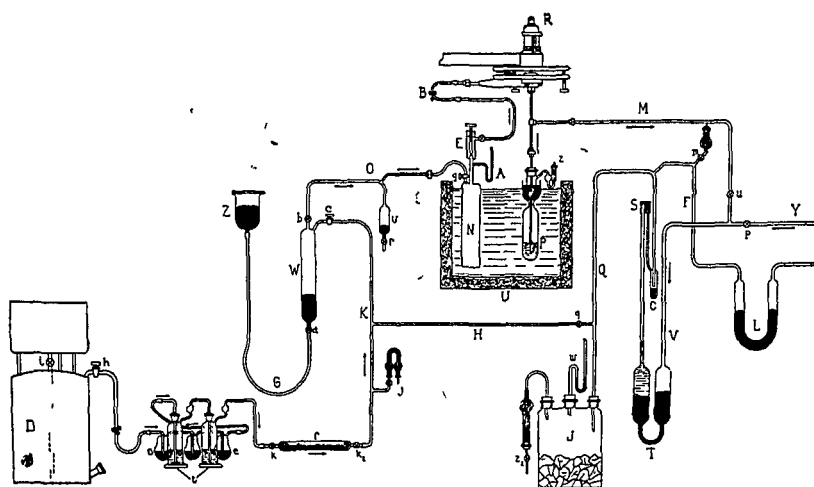


Fig. 1.

The nitrogen employed was prepared from a mixture of pure sodiumnitrite and ammoniumchloride, washed by distilled water, and collected in a gasometer $D$ (fig. 1). It was led through a series of wash-bottles $e$, filled with an alkaline solution of pyrogallol, then through others, filled with concentrated sulphuric acid ($t$), and finally through a tube $f$, containing a large surface of freshly sublimed ,phosphorous-pentoxide. The dried gas was preserved in a collector $W$, closed with dry mercury. When needed, it was pushed on into a metal reservoir $N$ by means of a movable mercury-holder $Z$. Any arbitrarily chosen pressure could be used which was then read on, the mercury-manometer $A$. The stopcock $E$ carries a micrometer, used in the regulation of the gas-current. In the study of the organic liquids, this reservoir $N$ was placed in the oil-thermostate $U$, with the glass-bulbs containing the liquids to be investigated. In this way the nitrogen was pro-heated to the temperature of observation, thus preventing disturbances of temperature in the surface-layer of the

liquid due to the small gas-bubbles emerging from the capillary tube.

The regulation of the velocity of flow of the gas was obtained by means of the stopcock $E$ already mentioned, in combination with two accurately adjustable pinch-cocks $B$, which were inserted between the reservoir $N$ and the apparatus $R$, carrying the capillary tube and its adjustments. With this arrangement no undesirable cooling of the surface, nor any lack of adjustment of the gas-velocity need be feared as a considerable source of error.

$b$. The apparatus $R$ consists of an upright rod $H$ (fig. $2a$), about 1 meter high, and made of brass heavily plated with nickel. It rests on a heavy iron tripod fitted with three levelling screws. The vertical rod can be rotated about its axis by means of two gliding discs $O$ at the foot of the pillar; they may be clamped fast when desired. In this way it is possible to bring the horizontal arm, bearing the adjusting arrangements and the movable counter-weight $I$ into any desired azimuth, and to fix its position by means of the clamps at $O$ and the collar at $H$. With the aid of a handle provided with a vertical rack and pinion, this horizontal arm can be raised to any height and fixed there with proper clamps. This arm can also be moved horizontally, in order to vary its length. Moreover it appeared to be necessary to prevent a slight bending of the pillar $H$ under certain circumstances, by means of three steel supports attached to $H$ and to the iron tripod [1]).

Just over $R$, it has at its end a rectangularly bent steel support, to which are attached the spiraltubes $G$, made of gas-tight aluminium-tubes, nearly 3 millimeters wide, and also the similar tubes $U$, which however consist of much wider spirals. The latter form the continuation of the aluminiumtubes $G$, and their ends are firmly fastened to the horizontal beam, which is fixed in the laboratory just above the whole apparatus. The two sets of spiraltubes appeared to be necessary to ensure the desired mobility of the apparatus with regard to the manometer-connecting tubes, and also to render an effective operation of the adjusting devices possible. The great sensitiveness of the manometer makes it necessary, that all the connecting tubes of the instrument, as well as the spirals $G$ and $U$, should be wrapped with a thick layer of white flannel or asbestos, in order to avoid the disturbing influence of slight oscillations of temperature.

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[1]) In the construction of this apparatus the mechanics D. VONK and A. VAN DER MEULEN, and the amanuensis J. J. FOLKERS, all of Groningen, have aided in a most practical and effective way.
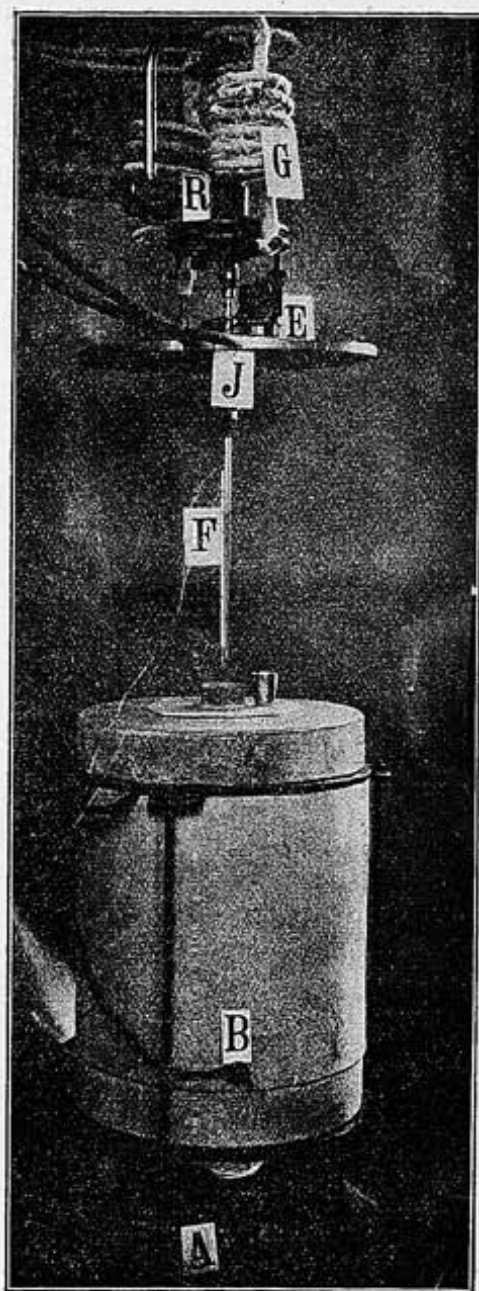
The adjusting device $R$ is represented on a somewhat larger scale, in fig. 2b; it is fixed in position over a resistance-furnace, and connected with the capillary tube made of the platinum-rhodium-alloy and the thermo-element $F$. In this drawing the rectangular support with the spirals $G$ are also plainly discernible, together with the hollow water-screen $J$, in which a current of cold water is continually circulating. This adjusting device consists of two semi-circular parts about 40 c.m. in diameter. One part is permanently attached to the apparatus $R$, the other can be fitted to it by means of pins and short tubes. The latter part has a circular glass-window, where upon the totally reflecting and movable (around a horizontal axis) prism $E$ is placed. By means of this prism the behaviour of the liquid in the furnace can be observed and controlled at every moment. At temperatures over 1000° C., coloured green glasses are inserted in front of the prism.

Fig. 2b.

With the protection of the waterscreen $J$ it proved possible, to use the manometer even at temperatures of 1650° C., without any disturbance from the heat-radiation of the furnace. The furnace $B$ is a platinum- (or nichrome-) resistance furnace of the usual type [1]; it has an inside wound heating-coil, and can be heated with a central tube of alundum inside, up to 1400° C., and without such a

[1] F. M. JAEGER, Anleitung u.s.w. (1913). p. 36.

central tube, to about 1680° C. The platinum-crucible is borne upon a movable support of burned magnesite, which can be fixed to the iron support $A$ at any elevation.

The construction and arrangement of the part $R$ of the adjusting device is elucidated more in detail in fig. 3a and 3b, a giving the
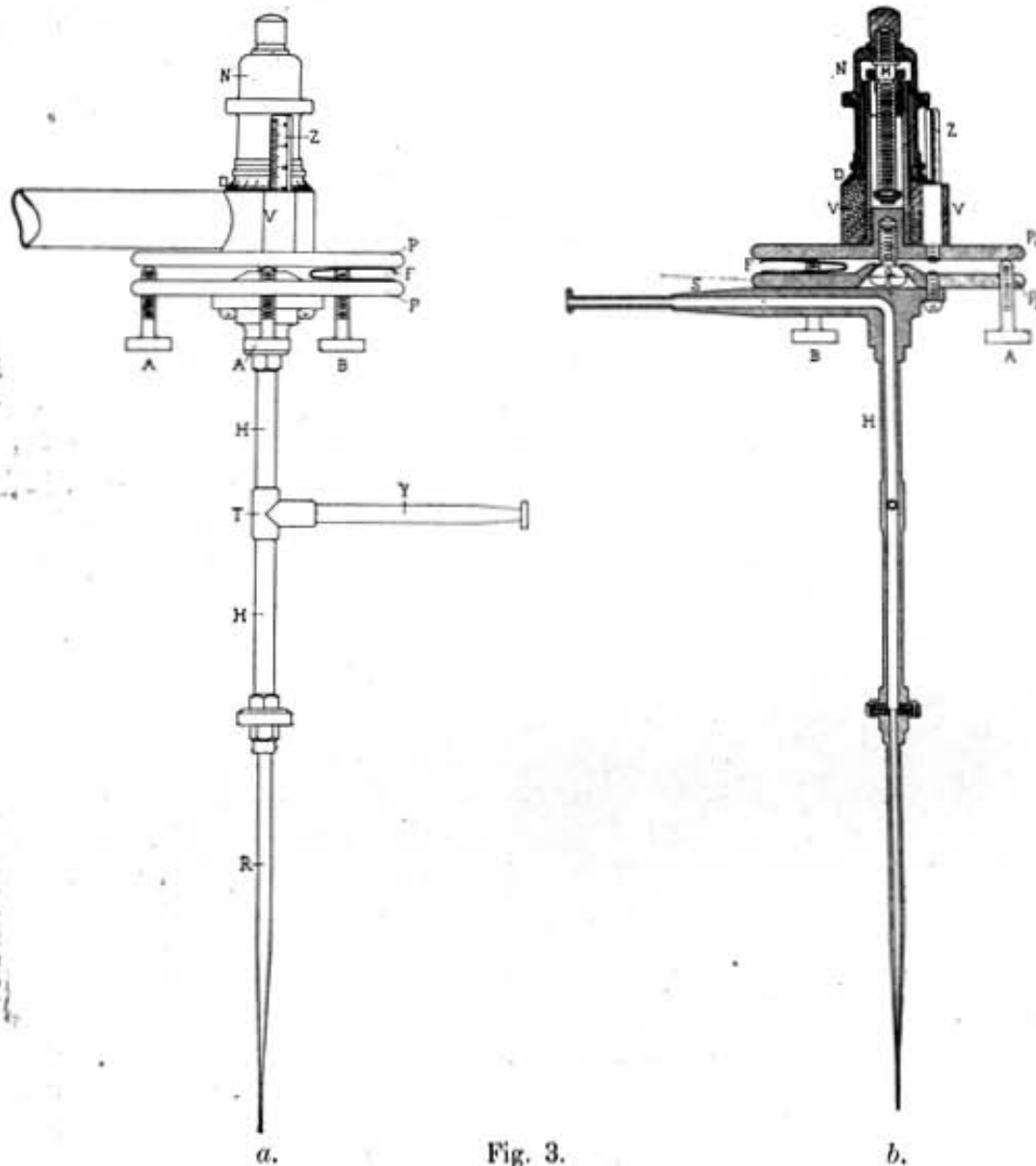
Fig. 3.

external view from one side, $b$ a section through it, in a plane, perpendicular to that of fig. 3a.

The apparatus consists of two metal discs $P_1$ and $P_2$, of which the disc $P_2$ with the tube $S$ attached to it, can be moved horizontally round the hemi-spherical button $Q$, and by means of the screws $A_1$ and $A_2$ can be brought to any inclined position with respect to

$P_1$. If $P_2$ is turned in a horizontal direction, the screws $A_1$ and $A_2$, as well as the springs $F_1$ and $F_2$, (fixed at one end only) will glide along the upper disc $P_1$, the whole upper part thus remaining in its original position. It appeared to be necessary to use a third screw $B$ for the adjustment of the capillary tube. It is first completely loosened from $P_1$, then after $P_1$ and $P_2$ have been brought into the desired relative position, the screw $B$ is turned so as to touch the disc $P_1$ slightly: in this way the relative position of the two plates is completely fixed. The tubes $S$ and $Y$, (not shown in fig. 3a) are bent rectangularly upwards, and fitted, to the spiral tubes $G$. By this arrangement an undesirable motion of the apparatus (during the adjustment of the capillary tube), due to the influence of the stress and weight of the connecting-tubes, could be sufficienly prevented, while the micrometerscrew $M$ at the same time remained in working condition. This screw $M$, fitted with a drum $N$ and a scale $D$, serves to move the discs $P_1$ and $P_2$ together through a known vertical distance. The screw has a pitch of 1 mm. exactly, the circumference being divided into one hundred equal parts, it thus permits a vertical motion of 0,01 mm. to be measured at $D$. This is more than sufficient, because experience proves, that no adjustment of the capillary tube in contact with the surface of the liquid, can be made with greater accuracy than about 0,1 mm. During this vertical motion the drum $N$ and the micrometerscrew $M$ remain in their original positions, because they can only move in a horizontal direction round the fixed part $V$ of the apparatus. A vertical scale $Z$, provided with divisions for about 30 mm., is moved at the same time with the two discs $P_1$ and $P_2$. In this way the number of revolutions of $N$ can be read directly. Concerning the adjustment of the capillary tube with respect to the surface of the liquid, which can be made either visually, or with the aid of the manometer-readings, the necessary directions will be given below.

§ 6. It was soon found, that the adjustment of the slight differences of pressure in the long connecting-tubes happened so slowly, that considerable errors in the measurements must inevitably occur. For this reason all the capillary tubes, with which the apparatus was originally equipped, were replaced by 5 mm. gas-tight tubes. These tubes were made in part of lead, in part of aluminium [1] and,

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[1] Also tubes of *cellon*, made by the *Rheinisch-Westphälische Sprengstoffe A.G.* in *Coln a/Rh.*, and which may be bent in hot water, can be recommended for such purposes. The material is gas-tight and fire-proof; however it is difficult to obtain it from the plant in any desired shape.

where necessary, were wrapped with a thick layer of asbestos. A considerable time had to be spent, to get all connections completely free from leakage; but when this was accomplished the indications of the manometer were so prompt as to be practically instantaneous. After this no errors from this source needed to be feared.

The connection of the tubes occurred in the usual way, as with high-pressure apparatus; these connections appeared to remain gastight, even after a longer use.

§ 7. For the measurement of the maximum pressures to be observed, originally a mercury-manometer of the type indicated by SCHEEL and HEUSE [1] was used. The instrument had been modified in some details; but it appeared not to be suitable for our work, because of the necessity of always reading *two* menisci, which was very troublesome with a pressure varying continually up to the moment, when the maximum was reached.

This instrument. therefore, which is very well adapted for static measurements, was only employed for the calibration of the manometer finally constructed. This second instrument was built on the principle of the manometer with two liquids.

In the measurements of organic liquids, it was necessary to avoid any contamination of the connecting-tubes with the vapour of the manometer-liquids, so that only pure *mercury* could be used as one of the liquids in the manometer. For the second liquid we chose normal *octane*. This liquid is very thin, behaves very well in contact with glass-walls, and, if completely dry, appeared not to blacken the mercury-surface, even after long exposure. The vapourtension at 20° C. is only 10,45 mm., the viscosity at 23° C. is 0,0052 C.G.S., the surface-tension at 25° C. is 21,3 Erg. pro cm$^2$., and the expansion-coefficient is 0,00118. After repeated fractional distillation, its boiling-point was found to be 125° C. under 758 mm. pressure, and its specific gravity at 25° C. was: $d_{4^0} = 0,6985$, i. e. about 19,38 times less than that of mercury at the same temperature. This last relation operates in the following way:

Suppose the diameter of the wider tube (fig. 4) to be $D$, that of the capillary tube $d$ and the mercury-meniscus to the right to be $a$ m.m. higher than to the left. Then the height of the octane-column to the left

[1] SCHEEL und HEUSE, Ein heizbares Quecksilbermanometer für Drucke bis 100 m.M.; Mitt. aus d. Phys. Techn Reichs-Anstalt, Zeits. f. Instr. **30**. (2). 45. (1910).

side $(c)$ is: $\dfrac{a}{\varepsilon}$ m.m., if $\varepsilon = \dfrac{1}{19,38} = 0{,}0516$. Suppose $\Delta p$ to be the increase

of pressure (in m.m. mercury), necessaryon the right side, to sink the mercury-surface just 1 m.m. The mercury-surface on the left side, will then rise just 1 m.m., and the octane-column from $c$ to $c'$ $(= \Delta h$ m.m.$)$, over $\dfrac{D}{d}$ m. m. The difference of level of the two mercury-surfaces is now: $(a-2)$ m.m., and the octane-column to the left $= \left(\dfrac{a}{\varepsilon} - 1 + \dfrac{D}{d}\right)$ mm. This corresponds to a mercury-column of:
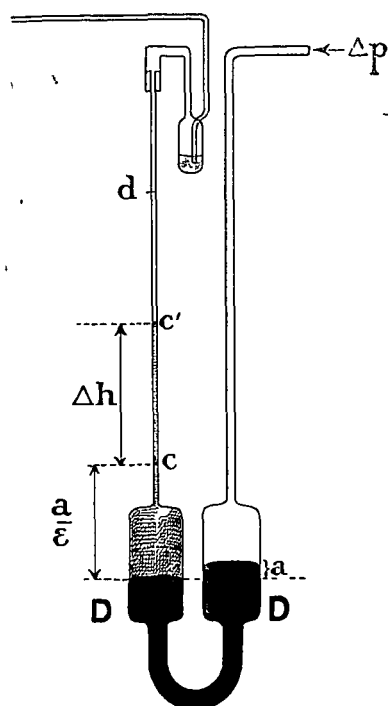
$$\left(\frac{a}{\varepsilon} - 1 + \frac{D}{d}\right)\varepsilon = \left(a - \varepsilon + \frac{D}{d}\varepsilon\right) \text{m.m.}$$

Therefore the necessary increase of pressure on the right side $(= \Delta p)$, is evidently:

$$\left(a - \varepsilon + \frac{D}{d}\varepsilon\right) - (a-2)\text{ m.m.} = 2 +$$

$$+ \varepsilon\left(\frac{D}{d} - 1\right)\text{ m.m., and thus:}$$



Fig. 4.

$$\frac{\Delta p}{\Delta h} = \frac{2 + \varepsilon\left(\dfrac{D}{d} - 1\right)}{\dfrac{D}{d}} = 2\frac{d}{D} + \varepsilon\left(1 - \frac{d}{D}\right) = \varepsilon + (2-\varepsilon)\frac{d}{D},$$

or:

$$\Delta p = \left\{\varepsilon + (2-\varepsilon)\frac{d}{D}\right\} \times \Delta h.$$

The reciprocal of the expression between $\{\}$ will be seen to be the "multiplication factor" $F$ of the instrument. With small values of $\varepsilon$, $(2-\varepsilon)$ will differ little from 2; therefore it is necessary to reduce $\dfrac{d}{D}$ as much as possible and to make $F$ as large as possible.

In our instrument these conditions were fulfilled in the following way: preliminary experiment gave $d = 2{,}406$ m.m$^2$, and $D = 1257{,}36$ m.m$^2$; thus $\dfrac{d}{D} = 0{,}00191$, and $F$ becomes ca. 18. The reproducibility of the same pressure appeared to be possible within a limit of

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0,1 m.m. octane, which corresponds to 0,005 m.m. mercury-pressure. The accuracy of the measurements was within the limits 0,05 and 0,1 °/₀; it was greater than necessary in comparison with the magnitude of the systematic errors of the method.

The final form of the manometer, as it was used in all the measurements is shown in fig. 5. This final form resulted from a great number of experiments and numerous changes. The tube $A$ is made
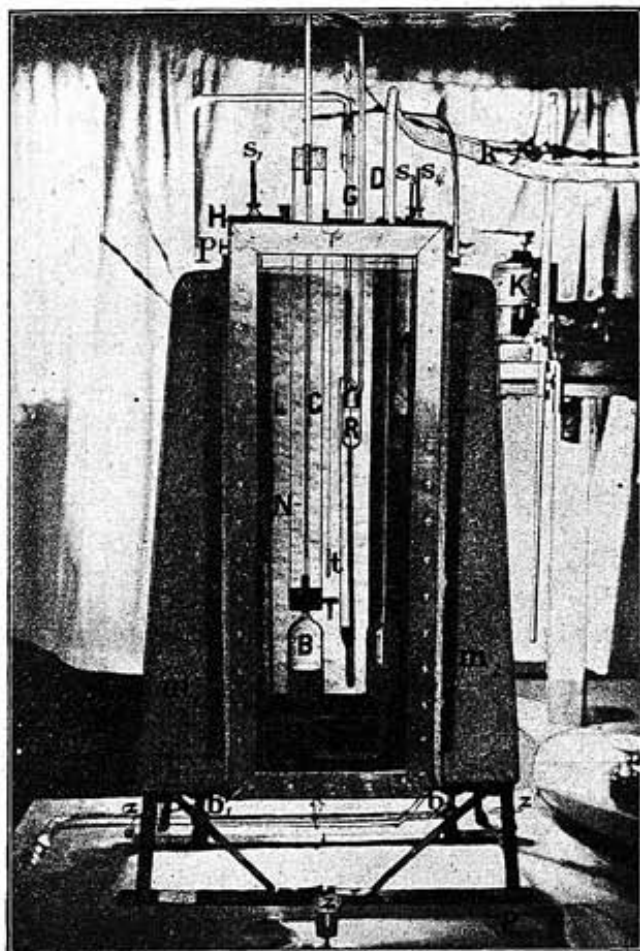


Fig. 5.

from the best quality of hard-glass, and connects two bulbs $B$ of ca. 39,9 mm. diameter with a volume of about 130 cubic centimeters; they possess 1,2 mm. wall-thickness. The bulbs must carefully be chosen, and be completely cylindrical throughout their full length. As the height is about 110 mm., it is not easy to find tubes of the desired quality. The capillary tube must have an internal diameter of about 1,7 or 1,8 mm., and a wall-thickness of about 2,5 mm., and must be suitable for precision-measurements and carefully

calibrated. Its length is about 600 mm. Another tube $D$, of equal length, but about 7 mm. in' diameter, serves as a connection to the gasapparatus. The capillary tube $C$ bears at its top a silver tube $E$, overlapping the tube $C$; it communicates with $C$ by means of a silver capillary tube, and can eventually be easily removed. The tube $C$ is widened at its top-end to about 10 mm.. and connected with the silvertube in such 'a manner, that no dust of the room can contaminate the capillary tube $C$, while at the other end it communicates with a small reservoir $R$, partially filled with octane ; — this for the purpose of preventing, as far as possible, the evaporation of the liquid in $C$. For this reason $R$ is placed in the same thermostat as the manometer-tube. The connection of $R$ with the atmosphere (or with the nitrogen) is made by means of an adjustable glass tube $G$, which opens into a very wide connecting tube leading to a large flask with three mouths, which is provided with dry calciumoxide, with a small manometer, a tube with drying materials and with a connection to the nitrogen-holder. In the fig. 1 the octane-reservoir is indicated by $C$, the silver capillary tube by $S$, the three-mouthed bottle by $J$. In the same way the manometer is indicated by $w$, the drying-tube by $z_2$, and the connecting tubes by $Q$ and $H$. The manometer is arranged in a 'glycerine-thermostat of the type usual in dilatometer-thermostats (Köhler), however its construction has been varied in some particulars. The thermostats commonly sold are quite unsuitable for this purpose, because they commonly show leakage or will show it very soon; then they cannot be used for glycerine, which was chosen because of its refractive index 'and' low volatility, because this liquid will dissolve the paste used in setting the glass-windows, within a short time. Two rectangular frames were therefore made of brass, about 3 cm. broad, and soldered to the thermostat. These frames were smoothed as perfectly as possible and possessed an inside furrow about 5 mm. deep and 1 cm. broad, in which a layer of very thin rubber paste, fixed by a solution of rubber' (in carbonbisulphide), held the two glasswindows fast. Then a second layer of plastic rubber was applied, and the second brass-frame was uniformly pressed against the former with some forty screws. The thermostat holds 22 kilos of glycerine, but even after long use it shows no leakage. By means of a toluene-regulator $T$, a spiral-stirrer $M$ with motor $K$, and a pair of small burners $b_1$ and $b_2$, the instrument is kept at $25°,1$ C. $\pm 0°,1$. '$L$ is a' thermometer, divided in $0°,1$ C. The support $F$ is suspended from the lid $H$ by means of four movable rods $l$. The manometertube can then be brought into a vertical 'position by means of the screws $s_1$, $s_2$, $s_3$ and $s_4$. Within

· 23*

the thermostat and just behind the capillary tube $C$ a glass-scale $N$ is introduced, which possesses a very accurate division in 0,2 mm., by means of very fine lines (3 microns) made by the Compagnie Génévoise. The scale is read with a telescope and ocular-micrometer by the same firm, and at a distance of about 2 Meters; the enlargement is about 25. During the readings the motor $K$ must be stopped for a moment, because even the slight vibrations are rather annoying. The thermostat is wrapped with felt except for the narrow opening needed for the readings. Behind the manometer a ground glass-plate is applied, which is illuminated by two long, tube-straight-filament incandescent-lamps, each of 50 candle power. Between the lamps and the thermostat, a watertank with glasswindows, is introduced, to prevent heat-radiation into the thermostat. With this mode of lighting the fine divisions and the octane-surface are seen very distinctly, without any observable parallax, against an illuminated background and readings can be made with extreme accuracy, with the aid of the movable cross-hair of the micrometer. However readings of less than 0,1 mm. appeared to be unnecessary, because of the fact, that the mean oscillations in the successive determinations of $H$, were about ± 0,05 mm. octane, the total uncertainty therefore being about 0,1 mm. octane-pressure, or about 0,005 m.m. mercury-pressure.

§ 8. To, bring the capillary tube into a vertical position, a mercurymirror was used: by means of the screws $A_1$ and $A_2$ (fig. 3b) the position of the capillary tube is altered until its mirrorimage will seem to be in a straight line with the tube; the position of $P_1$ and $P_2$ is then fixed by means of the screw $B$. The capillary tube itself was originally made from purest, iridiumfree platinum; this however appeared to be too soft, and so an alloy with 10°/₀ or 20°/₀ of rhodium was used afterwards. It is impossible to get any suitable capillary tubes for this purpose from the shops in trade. Therefore the rough capillary tube with its widened (ca. 6 mm.) upper part, was purveyed by HERAEUS; the lower end was then carefully turned off on the lathe to a conical and sharp edge, which was once more whetted on an oil-stone, if necessary.

With some practice in this way the repairs of the damaged or worn capillary tubes can be accomplished within a relatively short time; and it proved to be possible to obtain a cross section of the tube, which in several directions did not deviate more than about 0,002 m.m. from a pure circular shape, while the rim of the lower end measured no more than 0,01 m.m.

The cross section was determined by means of a horizontal

microscope, provided with a micrometer of the movable-cross-hairtype with divided cylinder: the diameters were measured in ten or twelve directions, the squares of these numbers added, the total amount divided by the number of measured diameters, and the square root from this value considered as the true value for $2r$. With regard to the measurements to be made at extreme temperatures, and on account of the fact, that a whetting of the capillary tubes appeared to be necessary almost after every set of measurements, no tubes with a radius of less than 0.040 c.m. were used during these investigations.

The platinum-rhodium-tube ends at its upperside in a carefully smoothed, polished brass disc; the tube of the adjustment-apparatus $R$ possesses just such a smoothed circular brass-plate. As a washer between the two discs, a very thin ring of mica is used; the capillary tube is screwed against the end of the apparatus $R$, and both tubes are then drawn together by the aid of two steel-keys, till the discs are firmly pressed against each other: in this way an absolutely gas-tight connection is obtained. This closure appears to be a very perfect one, and if it is often controlled, no leakage needs to be feared from this source.

§ **9.** The temperature-measurements were made with our calibrated thermo-couples and compensator-equipment, in the way always used in this laboratory [1]). Originally it was planned to connect the platinum-wire of the thermocouple directly to the end of the platinum-rhodium-tube by means of the oxygen-flame; this tube then being considered as the positive end of the thus obtained thermo-couple. However the perfect isolation of the tube at very high temperatures appeared to be a serious obstacle; so the idea was abandoned, and the usual thermo-couples, provided with isolating MARQUARDT-capillaries, was fixed to the platinum-rhodium-tube by means of fine platinum-wires; at the other end they were connected with the ice-box $Y$ (fig. 2a). The wires of the element are bare over a distance of about 5 c.m. from the junction; this point lies in the same horizontal plane as the lower end of the capillary tube, thus being in immediate vicinity of its opening. Of course all platinum parts within the furnace (crucibles, coils, etc.) need to be made from iridiumfree platinum, to prevent contamination of the thermo-couples as much as possible.

§ **10.** The adjustment of the capillary tube with respect to the

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[1]) F. M. JAEGER. Eine Anleitung u. s. w. (1913), vid. p. 16—24.

surface of the investigated liquid, can be made in the following way. The surface of the liquid is strongly illuminated, and now attentively the moment is watched, when the capillary tube, while screwed downwards, will just make contact with its mirror-image, seen in the surface of the liquid. At temperatures above 500° C. ordinarily not, and above 1000° C. never, a special illumination of the surface is necessary : for the liquid radiates then sufficiently to make the observation of the moment of contact a very accurate one. If the temperature however becomes 1400° or higher, it is often no longer possible to discern the end of the capillary tube from the surroundings : in these cases the adjustment must be made by the aid of the manometer, as is further below described in some details.

This visual method involves, even after sufficient practice an uncertainty of about 0.1 mm. in the case of organic liquids, which corresponds to ca. 0,006 to 0,008 mm. of mercury in the determination of the maximumpressure $H$. The percentage error of the observation caused thereby, is about from 0,4 to 0,7°/₀ ; this uncertainty in the adjustment of the capillary tube on the surface of the liquid, really appeared to be the chief source of the errors, as has been said, and is hardly or not to be avoided. However just at higher temperatures this and in the case of molten salts, where $H$ is very great, the accuracy of the method is only slightly affected by this uncertainty.

The other way of adjustment is this, that the capillary tube is approached quite near to the surface of the liquid ; then carefully a flow of nitrogen is applied, and then, while the capillary tube is slowly lowered by means of the micrometer-screw, by observation of the manometer, just the moment is determined in which a sudden rise of pressure, caused by the contact of the tube with the surface of the liquid, is seen. In this way the proposed aim was also often attained ; but the uncertainty appeared to be here of the same order of magnitude, as in the case of the visual method. Furthermore it is necessary to ascertain that the small column of liquid, which often remains hanging in the capillary tube, if turned upwards, has no misleading influence on this observation ; first this column of liquid needs to be blown out by the aid of a sufficiently strong flow of nitrogen, before the contact with the liquid is made in the way just described.

§ 11. The manometer was originally calibrated by immediate comparison with a mercury-manometer, which was read by means of a cathetometer and a divided scale. The paralaxis appeared to be extremely small ; the accurate adjustment of the mercury-surfaces

was highly facilitated, by putting a half transparent and diffusely illuminated screen behind the manometertube, on which screen black lines were drawn under an inclination of about 25° with the horizon in such a way, that their mirror-images in the mercury-surfaces were visible thereupon as a bundle of very fine and easily discernible dark lines. After the application of a certain excessive pressure to both manometers, two observers read *simultaneously* both instruments; the manometers were connected with each other by a short, very wide tube, sufficiently protected against temperature-oscillations. As an example of this calibration, the following series of observations may. be reproduced here in detail :

| *Mercury manometer.* | | | *Octane-manometer* (25° *C.*) |
|---|---|---|---|
| *Temperature :* | *Observed pressure :* | *Pressure at 0° C.* | *Rise of the octane column in m.m.* |
| 12,°4 | 7,00 | 6,99 | 124,8 |
| 12,°6 | 10,23 | 10,21 | 181,8 |
| 12,°9 | 12,45 | 12,43 | 220,8 |
| 12,°3 | 9,13 | 9,11 | 162,2 |
| 12,°6 | 13,14 | 13,12 | 235,3 |
| 13,°0 | 13,78 | 13,75 | 245,0 |
| 13,°1 | 12,44 | 12,42 | 219,9 |

A rise of the octane over 1 m.m. is therefore equivalent to an excessive pressure of 0,0561 $\pm$ 0,0003 m.m. mercury ($=74,8\pm0,4$ Dynes).

After it was found, that our measurements of the free surface-energy of purest *water*, were in so complete agreement with those of VOLKMANN, BRUNNER, WORLEY, among others, we afterwards repeated this calibration in most cases by the accurate determination of $\chi$ for pure water, at three or more temperatures: The factor of enlargement $F$ of the manometer appeared after all to be only slowly variable : in Octobre 1913 e.g. it was : 17,91 in February 1914 : 17,86; in June 1914 : 18,10; etc.

§ 12. The molten salts to be studied were in most cases placed into crucibles of iridium-free platinum; for the organic liquids we used vessels of glass of the shape indicated in fig. 7. A cylindrical glass tube $P$ with rounded bottom possesses a narrower neck at $A$; a wider glass cup $A$ is fixed round it. A tube $G$, closed with a stopper $K$, which is firmly fixed round the platinum capillary tube, possesses a collateral tube $B$, which ends into a drying tube $G$, which communicates with the free atmosphere at $Z$, and which is filled with

Fig. 7.

quick line. The vessel $P$ is cleaned, carefully dried, and if possible several times washed out with the vapours of the boiling liquid $V$; then it is filled again with a fresh quantity of the liquid $V$, while a layer of dry mercury is poured into $W$. The tube is placed into the oil thermostat, and the capillary tube with the part $GBC$ fixed to it, is lowered then, till $G$ makes contact with the surface of the mercury. If $V$ has reached a constant temperature, the capillary tube is further lowered by screwing it so far downwards, as is necessary to bring it just in contact with the surface of the liquid. This enclosure by means of mercury insures a sufficient freedom of motion, while the liquid at the same time can be shut off from the air [1]), and the small bubbles of nitrogen, emerging from $k$, can freely escape at $C$ and $Z_1$. All communications with the free atmosphere, which are present in the connecting tubes of fig. 1, are provided with drying apparatus, filled with dry calcium-oxide.

§ **13.** All measurements now were made in such a way, that always the zero-point was controlled anew accurately, before and immediately after each reading of the manometer. One needs to ascertain first, that all connecting tubes (fig. 6) are free from leakage, and that a diminution of the speed of gas-flow has *no* influence any longer on the value of the maximum pressure $H$. After the highest point of the octane-column is reached the liquid falls suddenly back to a point, which depends upon the speed of gas-flow, and then it begins to rise again slowly; etc. By experience one learns to estimate the reliability of the measurements, by the particular motion of the octane in the manometer; finally the reproducibility of the value of $H$ needs to be considered as the decisive criterion for answering the question, if the real pressure of equilibrium in the gas-bubble has been measured. Even when the speed of gas-flow is varied within certain limits, this value appears to be reproducible quite exactly. The influence of the variation of the depth of immersion $i$ on the manometer-readings, can be found by

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[1]) For if necessary, the air in the vessel $P$ can be first substituted by a current of pure nitrogen.

repeated lowering of the capillary tube over known distances by means of the micrometer-screw $N$ (fig. 3a), and by repeating the readings of the manometer in every case.

In all calculations we used the number **1333.2** Dynes as the equivalent of 1 m.m. mercury-pressure at 0° C.; the surface-energy is expressed in Erg pro c.m.². [1])

§ 14. As an illustration of the general availability of the method at all temperatures between — 80° C. and + 1650° C., we will give here already some few instances, relating to : *water*, some *colloidal solutions*, some *organic liquids*, and some *molten salts*. The specific weights of the organic liquids were, after a pycnometrical control at 25° C., calculated for other temperatures from the thermic expansion-formulae, if they were already sufficiently and accurately known in litterature.

In other cases the densities at 25°, 50°, and 75° C were pycnometrically determined, and a quadratic relation with three constants was calculated from these observations; this relation was used then afterwards for the determination of the other specific weights. In the case of the molten salts the specific weights must again be determined by means of a method to be described later. To use the numbers for the densities with more than three decimals, has no real significance, because the experimental errors are always of an order so as to make the influence of more decimals of no importance.

## § 15.

The curve (fig. 8) is evidently *concave* with respect to the temperature-axis ; the temperature-coefficient of $\mu$ is only small, and amounts to from 0,9 to 1,05 Erg. per 1° C.

Furthermore in this diagram the corresponding curves are repro-. duced for *a colloidal solution of iron-oxide* and for *a colloidal solution of silicium-dioxide* ; from both solutions the electrolytes were eliminated as far as possible by longer continued dialysation.

It appears, that both curves are evidently situated somewhat *above* that' for the pure solvent, although the deviations for $\chi$ from the values for pure water are only very small. The temperature-coefficients are analogous to those for the solvent itself; however in the case of the colloidal iron-oxyde it could be observed, that if such a solution was heated to a higher temperature, and if afterwards the determination of the surface-energy was repeated at the original

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[1]) The result is after all the same, as when expressed in "Dynes pro c.m.".

I.

| | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg. pro cm². | Specific gravity $d_{40}$ | Molecular Surface-energy $\mu$ in Erg. pro cm². |
|---|---|---|---|---|---|
| Temperature in ° C. | in mm. mercury of 0° C. | in Dynes | | | |

**WATER: $H_2O$.**

| Temperature in ° C. | in mm. mercury of 0° C. | in Dynes | Surface-tension $\chi$ in Erg. pro cm². | Specific gravity $d_{40}$ | Molecular Surface-energy $\mu$ in Erg. pro cm². |
|---|---|---|---|---|---|
| 0.4 | 2.593 | 3457 | 75.8 | 1.000 | 521.0 |
| 2 | 2 583 | 3444 | 75.5 | 1.000 | 518.9 |
| 16.4 | 2.498 | 3330 | 73.0 | 0.999 | 502.1 |
| 18.4 | 2.488 | 3317 | 72.7 | 0.999 | 500.0 |
| 25 | 2.456 | 3275 | 71.7 | 0.997 | 493.6 |
| 35 | 2.398 | 3197 | 70.0 | 0.994 | 483.1 |
| 37.8 | 2.383 | 3177 | 69.7 | 0 993 | 481.3 |
| 55 | 2.291 | 3055 | 66.9 | 0.986 | 464.3 |
| 74 2 | 2 178 | 2904 | 63.6 | 0.975 | 444.8 |
| 98.5 | 2.014 | 2688 | 58.9 | 0.960 | 415.8 |
| 99.9 | 2.004 | 2672 | 58.5 | 0.959 | 414.0 |

Molecular weight: **18.02.**    Radius of the Capillary tube: 0.04385 cm.
Depth: 0.1 mm.

The value of $\chi$ at 20° C. is thus **72.6** Erg. pro cm.²; it is more probable, than the often accepted value: **75.**[1] The here mentioned numbers are in full agreement with those of VOLKMANN[2] (1880), BRUNNER[3] (1847) and WORLEY[4] (1914); they differ however considerably from the values published by RAMSAY and SHIELDS[5].

lower temperature, for $\chi$ a value was found, somewhat different from the formerly observed one with a fresh solution. Thus, although the iron-oxide-solution remains "stable" until relatively higher temperature and in general does not coagulate on heating, it seems however yet to undergo some *irreversible* change, which is manifested by the somewhat changed value of the free surface-energy.

The described method is evidently also adapted for the investigation of *colloidal* solutions of different nature; it is planned to determine these values so highly important for the chemistry of the colloids in the case of a more extended series of colloidal substances.

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[1] FREUNDLICH, Kapillarchemie (1909), p. 28.
[2] VOLKMANN, Wied. Ann. 11, 177, (1880); 17, 353, (1882); 53, 633, 644, (1894); 56, 457, (1895); 62, 507, (1897); 66, 194, (1898).
[3] BRUNNER, Pogg. Ann. 70, 481, (1847).
[4] WORLEY, Journ. Chem. Soc. 105, 266, (1914).
[5] The other points mentioned in the diagram, have the following significance: $W$ = WEINBERG, Z. f. phys Chem. 10, 34, (1892); $S$ = SIEG, Diss. Berlin, (1887); $R$ = RAYLEIGH, Phil. Mag. (5), 30, 386, (1890); $Ss$ = SENTIS, Ann. de l'Univ. Grenoble, 9, 1, (1887); $H$ = PROCTOR HALL, Phil. Mag. (5), 36, 385, (1893); $M$ = MAGIE, Wied. Ann. 25, 421, (1885). These data were obtained by very different methods; they are evidently appreciably deviating from each other.

§ **16.** *Aliphatic Derivatives.*

II.

| | Maximum Pressure $H$ | | Surface-tension $\varkappa$ in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\mu$ in Erg pro cm². |
|---|---|---|---|---|---|
| Temperature in ° C. | in mm. mercury of 0° C. | in Dynes | | | |
| **ETHYLALCOHOL: $C_2H_5.OH$.** | | | | | |
| —79° | 1.066 | 1421.2 | 30.6 | 0.886 | 426.2 |
| —24 | 0.881 | 1174.5 | 25.2 | 0.820 | 369.6 |
| 0.1 | 0.825 | 1086.5 | 23.3 | 0.807 | 345.4 |
| 25 | 0.746 | 995.7 | 21.3 | 0.786 | 321.4 |
| 35 | 0.724 | 965.2 | 20.6 | 0.777 | 313.1 |
| 55 | 0.667 | 889.2 | 19.1 | 0.759 | 294.9 |
| 74.5 | 0.617 | 822.6 | 17.6 | 0.741 | 276.1 |

Molecular weight: **46.05.**     Radius of the capillary tube: 0.04385 cm.
Depth: 0 1 mm.

The alcohol was completely anhydrous and was therefore preserved in a bottle with drying-tube. At the boilingpoint (78°.4 C.) the value of $\varkappa$ is 17.0 Erg. pro cm². The mean temperature-coefficient of $\mu$ is only: **0.94** Erg.

III.

| | Maximum Pressure $H$ | | Surface-tension $\varkappa$ in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\mu$ in Erg. pro cm². |
|---|---|---|---|---|---|
| Temperature in ° C. | in mm. mercury of 0° C. | in Dynes | | | |
| **ACETIC ACID: $CH_3.COOH$.** | | | | | |
| 26° | 0.943 | 1257.2 | 27.0 | 1.046 | 401.7 |
| 34.6 | 0.914 | 1218.5 | 26.1 | 1.039 | 390.1 |
| 55 | 0.842 | 1122.3 | 24.0 | 1.022 | 362.7 |
| 70 | 0.787 | 1049.3 | 22.4 | 1.010 | 341.2 |
| 98.5 | 0.691 | 921.3 | 19.7 | 0.987 | 304.7 |

Molecular weight: **60.03.**     Radius of the capillar tube: 0.04385 cm.
Depth: 0.1 mm.

By repeated freezing and distilling, the liquid was thoroughly purified; its boilingpoint was 118°.1 C. The temperature-coefficient is between 26° and 55° C.: **1.3** and preserves that value up to the boilingpoint. At the last temperature the value of $\varkappa$ is: **17.7** Erg. pro cm².
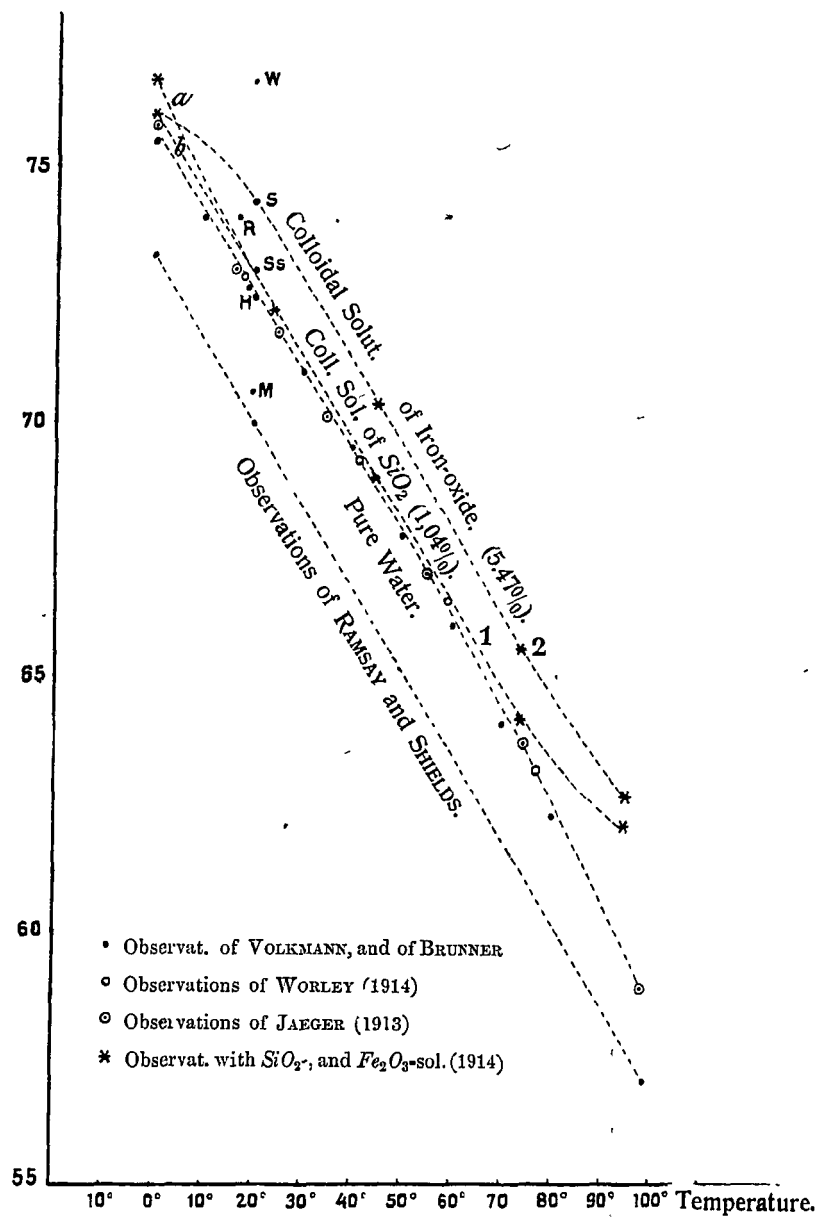
Fig. 8. Surface-tensions of pure water and colloidal solutions
at different temperatures.

Although acetic acid doubtless is a gradually dissociating liquid, and in accordance with this manifests only a small temperature coefficient ·of $\mu$, this last remains constant, contrary to the cases, where the curves appear to be concave or convex.

IV.

| | DIETHYLMALONATE: $COO(C_2H_5).CH_2.COO(C_2H_5)$. | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure, $H$ | | Surface-tension $\chi$ in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\nu$ in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| —19.9 | 1.237 | 1649.2 | 35.5 | 1.095 | 985.3 |
| 0.7 | 1.167 | 1555.8 | 33.5 | 1.075 | 941.2 |
| 8.5 | 1.142 | 1523.2 | 32.9 | 1.068 | 928.4 |
| 25.2 | 1.077 | 1435.9 | 31.0 | 1.050 | 884.8 |
| 34.5 | 1.044 | 1391.9 | 30.0 | 1.041 | 861.2 |
| 50.1 | 0.994 | 1325.2 | 28.5 | 1.025 | 826.6 |
| 69.2 | 0.920 | 1226.8 | 26.3 | 1.005 | 772.9 |
| 102 | 0.804 | 1071.8 | 23.0 | 0.969 | 692.5 |
| 124.5 | 0.723 | 963.9 | 20.6 | 0.945 | 630.7 |
| 144 | 0.660 | 880.2 | 18.8 | 0.924 | 584.3 |
| 148.7 | 0.649 | 866.4 | 18.5 | 0.919 | 577.1 |
| 171 | 0.571 | 761.6 | 16.2 | 0.896 | 513.9 |

Molecular weight: **160.1.**    Radius of the capillar tube: 0.04385 cm.
Depth: 0.1 mm.

The compound boiled constantly at 197°.3 C.; at —50° C. it is solidified. At the boilingpoint the value of $\chi$ is about: **13.7** Erg pro cm².; the temperature-coefficient of $\mu$ has as mean value: **2.52** Erg.

§ **17.** *Aromatic Derivatives.*

V.

| | BENZENE: $C_6H_6$. | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\mu$ in Erg. pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| 5.4 | 1 077 | 1436.7 | 30.9 | 0.895 | 607.7 |
| 9.5 | 1.055 | 1406.5 | 30.2 | 0.889 | 596.6 |
| 25.1 | 0.969 | 1291.9 | 27.7 | 0.873 | 553.8 |
| 35 | 0.920 | 1226.5 | 26.3 | 0.862 | 530.3 |
| 55 | 0.836 | 1114.6 | 23.8 | 0.841 | 487.8 |
| 74.6 | 0.757 | 1009.2 | 21.6 | 0.817 | 451.4 |

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

Although the mean value of the temperature-coefficient of $\mu$ oscillates round **2.0** Erg., the dependence of $\mu$ and $t$ is not a linear one: between 5° and 25° the coefficient is: **2.65**; between 25° and 55° C.: **2.12**; and between 55° and 75°: **1.95** Erg. At the boilingpoint (80.°5), the value of $\chi$ is: **20.7** Erg.

VI.

| ANISOL: $CH_3 . O . C_6H_5$. | | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\nu$ in Erg. pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| —21° | 1.375 | 1833.6 | 39.3 | 1.029 | 874.8 |
| 0.4 | 1.306 | 1741.7 | 37.3 | 1.010 | 840.6 |
| 25 | 1.210 | 1613.1 | 34.6 | 0.987 | 791.9 |
| 45 | 1.137 | 1516.5 | 32.5 | 0.970 | 752.5 |
| 74.4 | 1.022 | 1362.5 | 29.1 | 0.942 | 687.0 |
| 90.8 | 0.962 | 1282.2 | 27.4 | 0.927 | 653.9 |
| 110 | 0.875 | 1167.3 | 24.9 | 0.907 | 602.9 |
| 134.7 | 0.765 | 1020.2 | 21.7 | 0.882 | 535.3 |
| 151 | 0.700 | 932.9 | 19.8 | 0.865 | 494.8 |

Molecular weight: **108.6.**    Radius of the Capillar tube: 0.04352 cm. Depth: 0.1 mm.

The boilingpoint was constant at 151.°7 C.; at —50° the substance crystallizes to a beautiful, hard aggregate of crystals. The temperature-coefficient of $\nu$ increases, just as in the case of water, with increasing temperature: between —21° and 45° C. it is: **1.88**; between 45° and 90°.8 C. it is: ca. **2.14**; between 91° and 151° its mean value is: **2.63.**

VII.

| PHENETOL: $C_2H_5 . O . C_6H_5$. | | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\mu$ in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| —21° | 1.289 | 1718.5 | 36.8 | 1.006 | 902.1 |
| 0.3 | 1.213 | 1617.7 | 34.6 | 0.986 | 859.6 |
| 25.2 | 1.117 | 1489.0 | 31.8 | 0.962 | 803.1 |
| 45 | 1.037 | 1383.3 | 29.5 | 0.943 | 755.0 |
| 74.3 | 0.931 | 1240.8 | 26.4 | 0.914 | 689.9 |
| 90.6 | 0.875 | 1167.3 | 24.8 | 0.899 | 655.3 |
| 110 | 0.813 | 1084.6 | 23.0 | 0.889 | 612.3 |
| 134.7 | 0.734 | 979.0 | 20.7 | 0.855 | 565.6 |
| 150.1 | 0.687 | 915.9 | 19.3 | 0.849 | 529.8 |
| 160.5 | 0.651 | 868.6 | 18.3 | 0.839 | 506.3 |

Molecular weight: **122.1.**    Radius of the Capillar tube: 0.04352 cm. Depth: 0.1 mm.

The boilingpoint is constant at 168°; the substance solidifies at — 50° C. to an aggregate of long, colourless needles. The temperature-coefficient of $\nu$ can be considered as constant, its mean value being: **2.14** Erg.

VIII.

| ANETHOL: $CH_3O . C_6H_4 . CH : CH . CH_3 (1.4)$ | | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure | | Surface-tension $\chi$ in Erg pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\nu$ in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| *24.7 | 1.267 | 1689.2 | 36.2 | 0.988 | 1021.8 |
| *45.5 | 1.188 | 1583.8 | 33.9 | 0.969 | 969.1 |
| *75.1 | 1.078 | 1438.4 | 30.7 | 0.944 | 893.0 |
| *94.2 | 1.017 | 1355.7 | 28.9 | 0.927 | 850.9 |
| 115 | 0.929 | 1239.0 | 26.9 | 0.908 | 803.0 |
| 135.1 | 0.865 | 1153.4 | 25.0 | 0.890 | 756.4 |
| 160.9 | 0.787 | 1049.8 | 22.7 | 0.867 | 698.9 |
| 192.8 | 0.689 | 919.1 | 19.8 | 0.838 | 623.6 |
| 212.7 | 0.625 | 833.5 | 18.0 | 0.820 | 575.6 |
| 230 | 0.588 | 783.9 | 16.9 | 0.809 | 544.9 |

Molecular weight: **148.1.**   Radius of the Capillar tube: 0.04439 cm.; in the with * indicated observations, the radius was: 0.04352 cm. Depth: 0.1 mm.

The boilingpoint was constant at 230°.5 C.; the meltingpoint is: 21°5 C. Between 25° and 75° C. the temperature-coefficient of $\nu$ is about: **2.53**; later on it becomes fairly constant: **2.25.** At the boilingpoint the value of $\chi$ is: **1.68** Erg pro cm².

IX

| GUAJACOL: $CH_3O . C_6H_4 . OH (1,2)$. | | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\nu$ in Erg. pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| 26 | 1.377 | 1836.4 | 43.3 | 1.128 | 994.0 |
| 45.5 | 1.302 | 1736.4 | 40.9 | 1.109 | 949.6 |
| 66.5 | 1.224 | 1632.4 | 38.4 | 1.088 | 902.9 |
| 86 | 1.156 | 1540.7 | 36.2 | 1.068 | 861.8 |
| 106 | 1.087 | 1449.1 | 34.0 | 1.048 | 819.7 |
| 125 | 1.024 | 1365.8 | 32.0 | 1.029 | 780.9 |
| 146 | 0.954 | 1265.9 | 29.6 | 1.008 | 732.4 |
| 166 | 0.874 | 1166.0 | 27.2 | 0.988 | 682.1 |
| 184 | 0.803 | 1070.2 | 24.9 | 0.970 | 632.1 |
| 206 | 0.718 | 957.7 | 22.3 | 0.948 | 574.8 |

Molecular weight: **124.06.**   Radius of the Capillar tube: 0.04803 cm. Depth: 0.1 mm.

The substance boils under 24 mm. pressure at 106°.5 C.; the meltingpoint is 32° C. The temperature-coefficient of $\nu$ is between 26° and 46° C.: **2.17**; between 146° and 206° the curve is feebly convex to the $t$ axis and the mean value of the coefficient is therefore about: **2.66** Erg.

| RESORCINE-MONOMETHYLETHER : $C_6H_4(OH).(OCH_3)$ (1,3). | | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure $H$ | | Surface-tension $\lambda$ in Erg pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy in $\nu$ Erg pro cm². |
| | in mm. mercury of .° C. | in Dynes | | | |
| —20° | 2.622 | 3495.6 | 83.1 | 1.181 | 1850.1 |
| 0 | 1.636 | 2181.1 | 51.6 | 1.161 | 1161.9 |
| 25.9 | 1.462 | 1948.8 | 46.0 | 1.136 | 1051.0 |
| 45.9 | 1.380 | 1840.5 | 43.4 | 1.119 | 1001 6 |
| 66.5 | 1.318 | 1757.3 | 41.4 | 1.102 | 965.2 |
| 86.5 | 1.252 | 1669.7 | 39.3 | 1.082 | 927.5 |
| 107 | 1.196 | 1594.9 | 37.5 | 1.061 | 896.7 |
| 125 | 1.140 | 1519.9 | 35.7 | 1.044 | 862.9 |
| 146 | 1.075 | 1433.2 | 33.6 | 1.023 | 823.2 |
| 166 | 1 009 | 1345.0 | 31.5 | 1.003 | 782.0 |
| 184 | 0.956 | 1274.2 | 29.8 | 0.986 | 748 2 |
| 206 | 0.862 | 1149.4 | 26.8 | 0.965 | 682.6 |

Molecular weight: **124.06.**   Radius of the Capillary tube: 0.04803 cm.
Depth: 0.1 mm.

Under 25 mm. pressure, the compound has a boilingpoint of 144°C.
The observations over 180° C. relate to the substance already slightly dissociated, as was seen from the brownish colour of the liquid. At —79° C. it becomes glassy, without indication of crystallisation. At 0° and — 20° C. also, the viscosity of the liquid is still enormous.

XI.

| RESORCINE-DIMETHYLETHER : $C_6H_4(OCH_3)_2$ (1, 3). | | | | | |
|---|---|---|---|---|---|
| Temperature in 0° C. | Maximum Pressure $H$ | | Surface-tension $\lambda$ in Erg pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\nu$ in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| —22° | 1.520 | 2026.5 | 44.3 | 1.104 | 1107.9 |
| 0 | 1.419 | 1892.3 | 41.3 | 1.084 | 1045.6 |
| 25 | 1.325 | 1766.2 | 38.6 | 1.064 | 989.4 |
| 45.3 | 1.250 | 1667.0 | 36.4 | 1.046 | 944.3 |
| 70.5 | 1.166 | 1554.4 | 33.9 | 1.022 | 893.2 |
| 90.1 | 1.090 | 1453.2 | 31.7 | 1.004 | 844.6 |
| 116 | 1.007 | 1342.7 | 29.2 | 0.980 | 790 6 |
| 135 3 | 0.943 | 1257.0 | 27.3 | 0.963 | 747.9 |
| *162.1 | 0.781 | 1041.0 | 24.4 | 0.939 | 679.8 |
| *189.9 | 0.700 | 932.8 | 21.8 | 0.914 | 618 4 |
| *210 | 0.637 | 849.5 | 19.8 | 0.894 | 570.0 |

Molecular weight: **138.08.**   Radius of the Capillary tube: 0.04439 cm.; in the with * indicated observations the radius was: 0.04803 cm.
Depth: 0.1 mm.

The substance has a constant boilingpoint at 214°.5 C.; the liquid can be undercooled to — 76° C., and solidifies to a crystal-aggregate, wich melts at —52° C. At lower temperatures, as far as to 0° C., the temperature-coefficient of $\nu$ is rather large: **2.83** Erg; later it is fairly constant, with the value: **2.25** Erg.

## XII.

| HYDROCHINON-DIMETHYLETHER: $C_6H_4(OCH_3)_2$ (1, 4). | | | | | |
|---|---|---|---|---|---|
| Temperatuur in ° C. | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg pro cm. | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\nu$ in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| 66° | 1.106 | 1474.5 | 34.7 | 1.036 | 905.4 |
| 86.5 | 1.031 | 1374.1 | 32.3 | 1.008 | 858.3 |
| 106 | 0.974 | 1299.2 | 30.5 | 0.990 | 820.3 |
| 126 | 0.909 | 1213.8 | 28 4 | 0.976 | 771.1 |
| 146 | 0.843 | 1124.4 | 26.4 | 0.957 | 726.2 |
| 166 | 0.775 | 1032.7 | 24.2 | 0 938 | 674.7 |
| 184 | 0.709 | 945.3 | 22.1 | 0.921 | 623.7 |
| 206 | 0.628 | 837.0 | 19.5 | 0.901 | 558.4 |

Molecular weight: **138.08.** Radius of the Capillary tube: 0.04803 cm. Depth: 0.1 mm.

The meltingpoint of the substance is at 56° C.; it boils under a pressure of 20 mm., at 109° C. On cooling first a glass is obtained, which gradually crystallizes in fine needles. Between 66° and 106° the temperature-coefficient of $\nu$ is about: **2.11**; between 106° and 166°, about: **2.46**; and between 166° and 206° C., about: **2.88** Erg. The relating curve is therefore concave to the $t$-axis.

## § 18. Heterocyclic Derivatives.

### XIII.

| PYRIDINE $C_5H_5N$. | | | | | |
|---|---|---|---|---|---|
| Temperature in ° C. | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg in cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| —79° | 1.698 | 2263.8 | 48.9 | 1.078 | 827.8 |
| —20.5 | 1.430 | 1906.5 | 41.1 | 1.018 | 722.9 |
| 0.1 | 1.329 | 1771.8 | 38.1 | 0.998 | 679.0 |
| 25 | 1.215 | 1619.8 | 34.9 | 0.975 | 631.8 |
| 35 | 1.177 | 1569.2 | 33.8 | 0.962 | 607.3 |
| 55 | 1.099 | 1465.2 | 31.5 | 0.942 | 583.4 |
| 74 | 1.022 | 1362.5 | 29.3 | 0.923 | 550.1 |
| 92.5 | 0.960 | 1279.9 | 27.5 | 0.904 | 523.5 |

Molecular weight: **75.09.** Radius of the Capillary tube: 0.04385 cm. Depth: 0.1 mm.

. The pyridine crystallizes readily at —52° C.; thus the measurements at —79° C. relate to a strongly undercooled liquid. The curve, giving the dependence of $\nu$ and $t$ is not quite regular. At the boilingpoint (114°.5 C.), the value of $\chi$ is: **25.2** Erg pro cm².

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## XIV.

| | Maximum Pressure $H$ | | Surface-tension $\chi$ | Specific | M( |
|---|---|---|---|---|---|
| Temperature in $^\circ$ C. | in mm. mercury of 0° C. | in Dynes | in Erg pro cm². | gravity $d_{4^o}$ | S er i |

α-Picoline: $C_5H_4(CH_3)N$.

| Temperature in $^\circ$ C. | in mm. mercury of 0° C. | in Dynes | in Erg pro cm². | gravity $d_{4^o}$ | |
|---|---|---|---|---|---|
| —70° | 1 505 | 2007.1 | 47 4 | 1.036 | |
| —20.7 | 1.246 | 1661.5 | 39.2 | 0.986 | |
| 0 | 1.165 | 1553.2 | 36.6 | 0.965 | |
| 25.8 | 1.074 | 1432.4 | 33.7 | 0.940 | |
| 46 | 0.999 | 1332.5 | 31.3 | 0.920 | |
| 66.5 | 0.928 | 1236.9 | 29.0 | 0 900 | |
| 86.5 | 0.846 | 1128.5 | 26 4 | 0.881 | |
| 106 | 0.787 | 1049.3 | 24.6 | 0.862 | |
| 126 | 0.718 | 957.7 | 22.5 | 0.842 | |

Molecular weight: **93.07.** Radius of the Capillary tube: 0.048
Depth: 0.1 mm.

The liquid, which is boiling constantly at 133°.5 C., can be cooled as far as — 74° C.; it solidifies at — 64° C. and melti very rapidly. Between — 70° and — 21°, the temperature-coe is about: **2.83**; afterwards the mean value remains about: **2.(**

## XV.

Chinoline: $C_6H_4.N.C_3H_3$.

| Temperature in $^\circ$ C. | Maximum Pressure $H$ | | Surface-tension $\gamma$ | Specific | M( |
|---|---|---|---|---|---|
| | in mm. mercury of 0° C. | in Dynes | in Erg. pro cm². | gravity $d_{4^o}$ | S ene Erg |
| —21° | 1.682 | 2242.4 | 49.1 | 1.124 | 1 |
| 0 | 1.608 | 2143.8 | 47.0 | 1.108 | 1 |
| *24.8 | 1.562 | 2082 5 | 44 7 | 1.089 | 1 |
| *45 2 | 1.486 | 1981.1 | 42 5 | 1.073 | 1 |
| *74.3 | 1 379 | 1838.2 | 39.4 | 1.051 | |
| *94.7 | 1.303 | 1737.1 | 37.2 | 1.034 | |
| 115 | 1.210 | 1613.0 | 35.2 | 1.018 | |
| 135·2 | 1.135 | 1513.8 | 33.0 | 1.002 | |
| 160 | 1.047 | 1395.9 | 30 4 | 0.981 | |
| 192.5 | 0.929 | 1239.0 | 26.9 | 0.954 | |
| 213 | 0.855 | 1139.9 | 25 7 | 0.938 | |
| 230 | 0.797 | 1063.3 | 23.0 | 0.924 | |

Molecular weight: **129.07.** Radius of the Capillary tube: 0.044!
in the with * indicated observatioi radius was: 0.04352 cm.
Depth: 0.1 mm.

The boilingpoint was constant at 233° C.; the liquid can be cooled as far as —50°, and then crystallizes, melting readily at – The temperature-coefficient of ᵘ increases with the tempei between —21° and 45° C. it is: **1.92;** between 45° and 115° C. between 115° and 230°: **2.33** Erg. At the boilingpoint the valu is: **22.7** Erg. pro cm².

Molecular Surface-
energy, in Erg pro c.m².

Fig. 9.



Temperature

24*
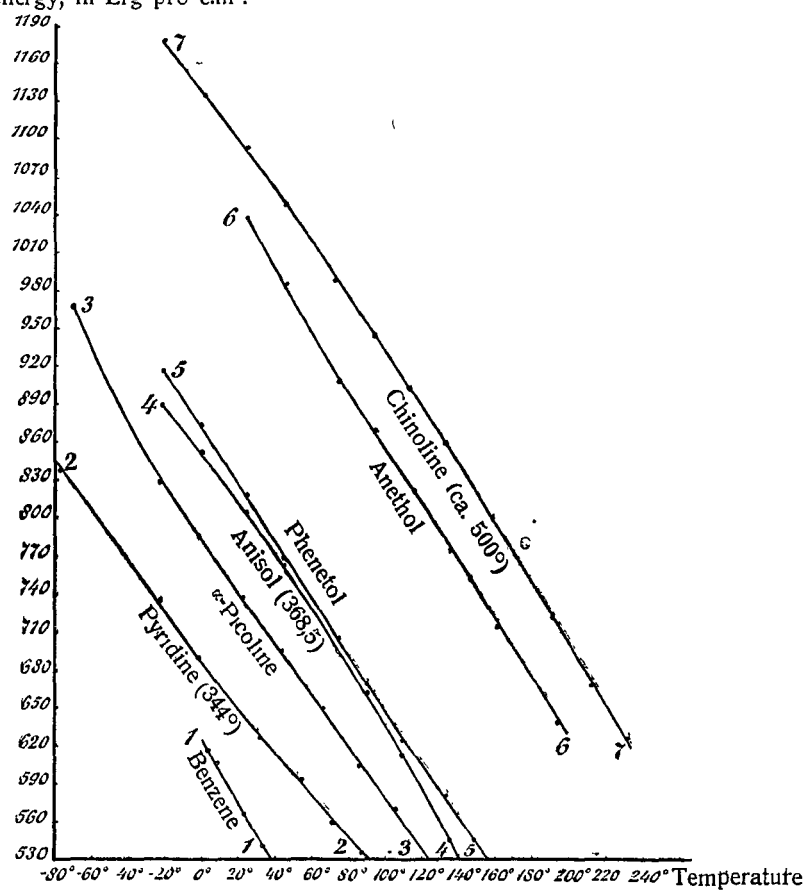
Some of the curves, which relate to these organic liquids, are reproduced here in the usual graphical way (fig. 9); the corresponding critical temperatures of the liquids, so far as they are known, are mentioned and written between ( ) behind the names of the substances investigated.

## 19. Salts of the Alkali-Metals.

### XVI.

| POTASSIUMCHLORIDE : $KCl$. | | | | | |
|---|---|---|---|---|---|
| Temperature in °C. (corr. on G. Th.) | Maximum Pressure $H$ | | Surface-tension $\chi$ in Erg pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\mu$ in Erg pro cm². |
| | in mm. mercury of 0° C. | in Dynes | | | |
| 799.5 | 3.015 | 4019 | 95.8 | 1.509 | 1290.0 |
| 827.1 | 2.957 | 3942 | 94.0 | 1.492 | 1275.3 |
| 861.5 | 2.873 | 3830 | 91.3 | 1.470 | 1251.0 |
| 885.1 | 2.819 | 3758 | 89.7 | 1.456 | 1237.0 |
| 908.5 | 2.768 | 3690 | 88.0 | 1.442 | 1221.3 |
| 941 | 2.697 | 3595 | 85.8 | 1.421 | 1202.6 |
| 986 | 2.582 | 3442 | 82.2 | 1.396 | 1165.8 |
| 1029 | 2.484 | 3311 | 79.1 | — | — |
| 1054 | 2.425 | 3233 | 77.2 | — | — |
| 1087.5 | 2.361 | 3147 | 75.2 | — | — |
| 1103.6 | 2.313 | 3083 | 73.7 | — | — |
| 1125 | 2.275 | 3033 | 72.5 | — | — |
| 1167 | 2.182 | 2909 | 69.6 | — | — |

Molecular weight: **74.56.**  Radius of the Capillary tube: 0.04736 cm. at 15° C. The expansion-coefficient is here 0.0000083.
Depth: 0.1 mm.

The salt melts sharply at 771° C.; after four hours heating between 900° and 1100°, it solidifies at 769° C. It evaporates rapidly at 980°, at 1160° with great speed. Just as in the case of the other alkali-salts, the vapours are doubtlessly acid, while the solidified mass gives an alkaline reaction. if dissolved in water. The gradual dissociation lowers the value of the maximum piessure more and more, as is seen from repeated experiments after a longer heating 1100° C.

As some illustrations of the changes caused by the commenced dissociation of the salt, the following measurements are given, which were made after a heating at 850° and 1150° C. during full four hours:

At 848° C. the maximumpressure was found to be 2.821 mm. mercury
„ 904 „ „ „ „ „ „ „ „ 2.720 „ „
„ 941 „ „ „ „ „ „ „ „ 2.645 „ „
„ 956.5 „ „ „ „ „ „ „ „ 2.615 „ „
„ 1037 „ „ „ „ „ „ „ „ 2.455 „ „

All values are evidently lower than the previously observed ones, and at the lower temperatures, at which the observations were made after the longest heating of the salt, the decrease is most appreciable.

XVII.

| POTASSIUMBROMIDE: $KBr$. | | | |
|---|---|---|---|
| Temperat.<br>in ° C.<br>(corr.) | Maximum Pressure $H$ | | Surface-<br>tension $\chi$ in<br>Erg. pro cm². |
| | in mm.<br>mercury of<br>0° C. | in Dynes | |
| 775° | 2.702 | 3602 | 85.7 |
| 798 | 2.642 | 3522 | 83.8 |
| 826 | 2.585 | 3446 | 82.0 |
| 859 | 2.504 | 3338 | 79.5 |
| 886.5 | 2.450 | 3266 | 77.8 |
| 920 | 2.376 | 3167 | 75.4 |

Molecular weight **119.02**.
Radius of the Capillary tube : 0.04728 cm. at 15° C.
Depth : 0.1 mm.

The dissociation and splitting off of hydrogen-bromide and bromine is observed at 825° C. At 940° C. the evaporisation and dissociation of the salt have become so rapid, that measurements at higher temperatures seemed to be without any real significance.

XVIII.

| POTASSIUM IODIDE: $KJ$. | | | |
|---|---|---|---|
| Temperat.<br>in ° C.<br>(corr. on<br>G. Th.) | Maximum Pressure $H$ | | Surface-<br>tension $\chi$<br>in Erg<br>pro cm². |
| | in mm.<br>mercury of<br>0° C. | in Dynes | |
| 737° | 2.372 | 3162 | 75.2 |
| 764 | 2.274 | 3031 | 72.1 |
| 812 | 2.183 | 2910 | 69.2 |
| 866 | 2.106 | 2807 | 66.8 |
| 873 | 2.097 | 2795 | 66.5 |

Molecular weight: **165.96**.
Radius of the Capillary tube: 0.04728 cm. at 15° C.
Depth: 0.1—0.2 mm.

The salt melts at ca. 700° C. Already at 750° C. it evaporates rather rapidly, and at 900° C. with dissociation into hydrogen-iodide and iodine. Measurements at higher temperatures can have hardly any significance.

XIX.

| | | Sodiumchloride : NaCl. | | | |
|---|---|---|---|---|---|

| Temperature in ° C. (corr. on G. Th.) | Maximum Pressure H | | Surface-tension / in Erg. pro cm². | Specific gravity $d_{4^0}$ | Molecular Surface-energy $\mu$ in Erg. pro cm². |
|---|---|---|---|---|---|
| | in mm. mercury of 0° C. | in Dynes | | | |
| 802.6 | 3 580 | 4772 | 113.8 | 1.554 | 1275.9 |
| 810.5 | 3.572 | 4762 | 113.5 | 1.549 | 1275.4 |
| 820.8 | 3.552 | 4735 | 112.9 | 1.543 | 1270.8 |
| 832 | 3.520 | 4692 | 111.9 | 1.537 | 1262.6 |
| 859 | 3.457 | 4608 | 109.9 | 1.523 | 1247.7 |
| 883 2 | 3.401 | 4534 | 108.2 | — | — |
| 907 5 | 3.345 | 4459 | 106.4 | — | — |
| 930.6 | 3.285 | 4379 | 104.5 | — | — |
| 960.5 | 3.227 | 4302 | 102 7 | — | — |
| 995.5 | 3.132 | 4175 | 99.7 | — | — |
| 1037 | 3.047 | 4062 | 97.0 | — | — |
| 1080 | 2.951 | 3934 | 94.0 | — | — |
| 1122.3 | 2.864 | 3818 | 91.3 | — | — |
| 1171 8 | 2.761 | 3681 | 88.0 | — | — |

Moleculair weight: **58.46**   Radius of the Capillary tube: 0.04736 cm. at
15° C
Depth: 0.1 mm.

The pure salt melts at 801° C. At 1080° it evaporates already rapidly, at 1150° C. very rapidly. The temperature-coefficient of $\mu$ calculated in the few cases, where values of specific gravity were available, is very small. about **0.57** Erg. The solidified mass gives in water a rather strong alkaline reaction; the vapours of the heated salt have an acid reaction.

## XX.

| | | Maximum Pressure $H$ | | Surface- |
|---|---|---|---|---|
| Temperature in ° C. | (corr. on G. Th.) | in mm. mercury of 0°C. | in Dynes | tension $\chi$ in Erg pro cm². |

**SODIUMSULPHATE: $Na_2SO_4$.**

| 900° | 6.285 | 8379 | 194.8 |
|---|---|---|---|
| 945 | 6.247 | 8328 | 189.3 |
| 990 | 6 209 | 8278 | 188.2 |
| 1032 | 6.149 | 8197 | 186.5 |
| 1077 | 6 088 | 8116 | 184.7 |

Molecular weight: **142.07.**
Radius of the Capillary tube: 0.04512 cm.
Depth: 0.1 mm.

The pure salt melts at 884° C. If heated to 1100° C. the solidified mass' gives in water a rather strong alkaline reaction, indicating a dissociation. Measurements at higher temperatures than 1100° C. thus seemed to be useless.

## XXI.

**SODIUMMOLYBDATE: $Na_2MoO_4$.**

| | | Maximum Pressure $H$ | | Surface- |
|---|---|---|---|---|
| Temperature in ° C. | (corr.) | in mm. mercury of 0° C. | in Dynes | tension $\chi$ in Erg pro cm². |

| 698.5° | 6.091 | 8122 | 214.0 |
|---|---|---|---|
| 728.5 | 5.975 | 7967 | 210.0 |
| 751 | 5.921 | 7893 | 208.1 |
| 777 | 5.828 | 7770 | 204 9 |
| 818.8 | 5.757 | 7675 | 202.4 |
| 858.5 | 5.657 | 7542 | 199.0 |
| 903.8 | 5.552 | 7401 | 195.4 |
| 948 | 5.436 | 7247 | 191.4 |
| 989 5 | 5.330 | 7106 | 187.7 |
| 1035 | 5.224 | 6966 | 184.1 |
| 1078.5 | 5.141 | 6854 | 181 2 |
| 1121.5 | 5.070 | 6760 | 178.8 |
| 1171.5 | 4.998 | 6654 | 176.1 |
| 1212 | 4.947 | 6595 | 174.6 |

Molecular weight: **206.**
Radius of the Capillary tube: 0.05240 cm.
Depth: 0.1 mm.

The compound melts at 687° C. to a colourless liquid.

| Temperature in ° C. (corr.) | Maximum Pressure $H$ | | Surface-tension $\chi$ |
|---|---|---|---|
| | in mm. mercury of 0° C. | in Dynes | in Erg pro cm². |
| 860° | 6.361 | 8481 | 223.8 |
| 873.5 | 6.342 | 8455 | 223.1 |
| 897 . | 6.303 | 8403 | 221.8 |
| 923 | 6.256 | 8341 | 220.2 |
| 962.5 | 6·169 | 8224 | 217.4 |
| 976.8 | 6.146 | 8194 | 216.4 |
| 1001.2 | 6.099 | 8132 | 214.8 |
| 1038.5 | 6.027 | 8035 | 212.3 |
| 1057 | 5.987 | 7982 | 211.0 |
| 1074 | 5.953 | 7936 | 209.8 |
| 1089.5 | 5.923 | 7897 | 208.8 |
| 1112 | 5.879 | 7838 | 207.3 |
| 1156.5 | 5.791 | 7720 | 204.2 |
| 1167.5 | 5.766 | 7687 | 203.4 |
| 1183.5 | 5.737 | 7649 | 202.4 |
| 1192.2 | 5.718 | 7624 | 201.8 |
| 1214 | 5.675 | 7566 | 200.3 |

Molecular weight: **109.94.**
Radius of the Capillary tube:
0.05240 cm. at 16° C.
Depth: 0.1 mm.

The salt was prepared from purest lithium-carbonate and sulfuric acid, carefully dried and heated at 900° C.; it melts at 849° C. After being heated to 1200° C., the substance, shows an alkaline reaction with water. Also here it is of little significance, to pursue the measurements to higher temperatures.

XXIII.

LITHIUMMETASILICATE: $Li_2SiO_3$.

| Temperature in ° C. (corr. on G.Th.) | Maximum Pressure $H$ | | Surface-tension $\chi$ |
|---|---|---|---|
| | in mm. mercury of 0° C. | in Dynes | in Erg pro cm². |
| 1254° | 11.82 | 15759 | 374.6 |
| 1380 | 11.29 | 15052 | 358.2 |
| 1421 | 11.22 | 14958 | 356.2 |
| 1479 | 11.11 | 14812 | 352.8 |
| 1550 | 10.97 | 14626 | 348.7 |
| 1601 | 10.90 | 14532 | 346.6 |

Molecular weight: **90.01.**
Radius of the Capillary tube: 0.04706 cm.
Depth: 0.1—0.2 mm.

The analysed metasilicate was perfectly pure. It melts at 1201° C. The temperature-coefficient of $\mu$ is very small.
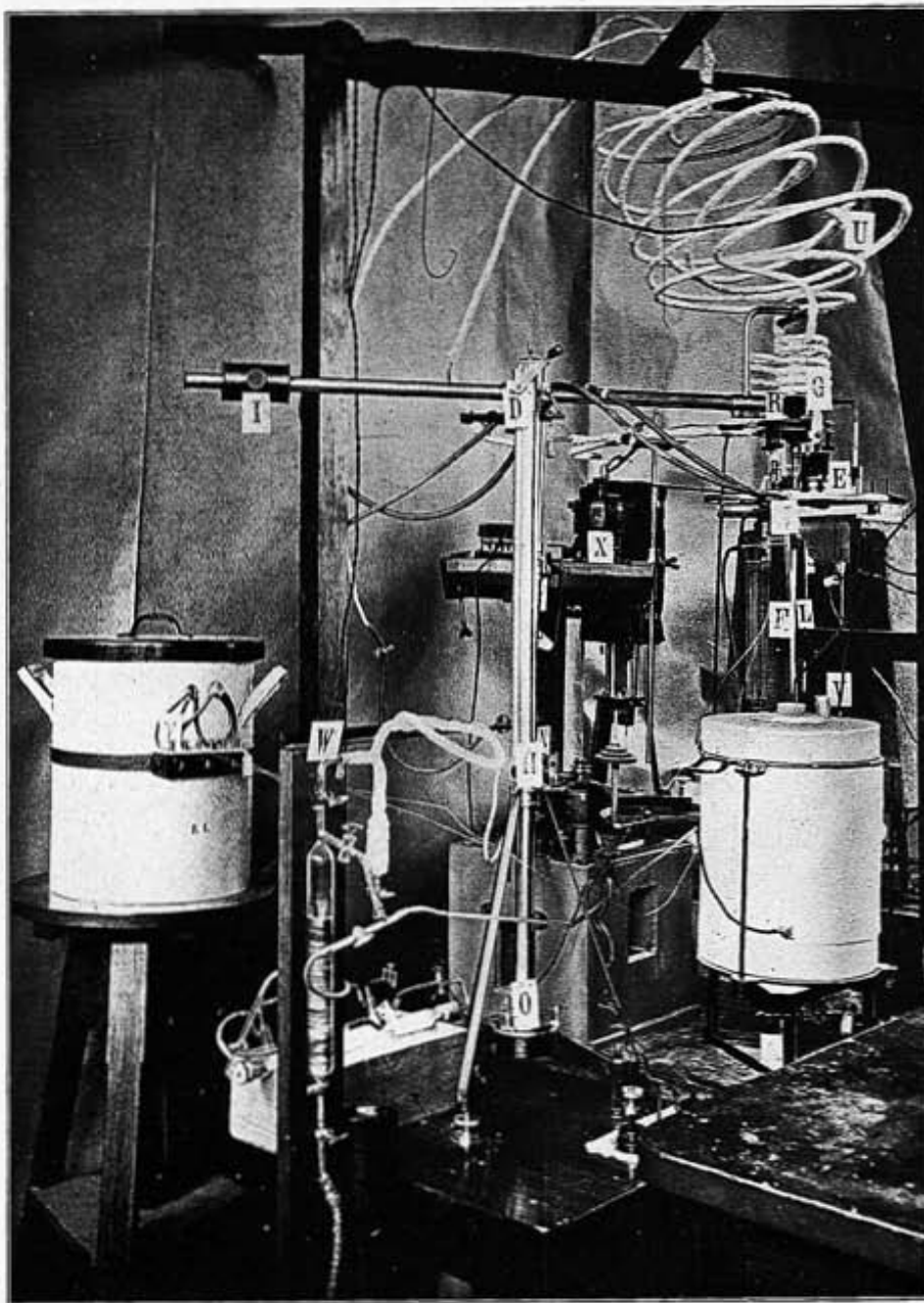
Fig. 2a.
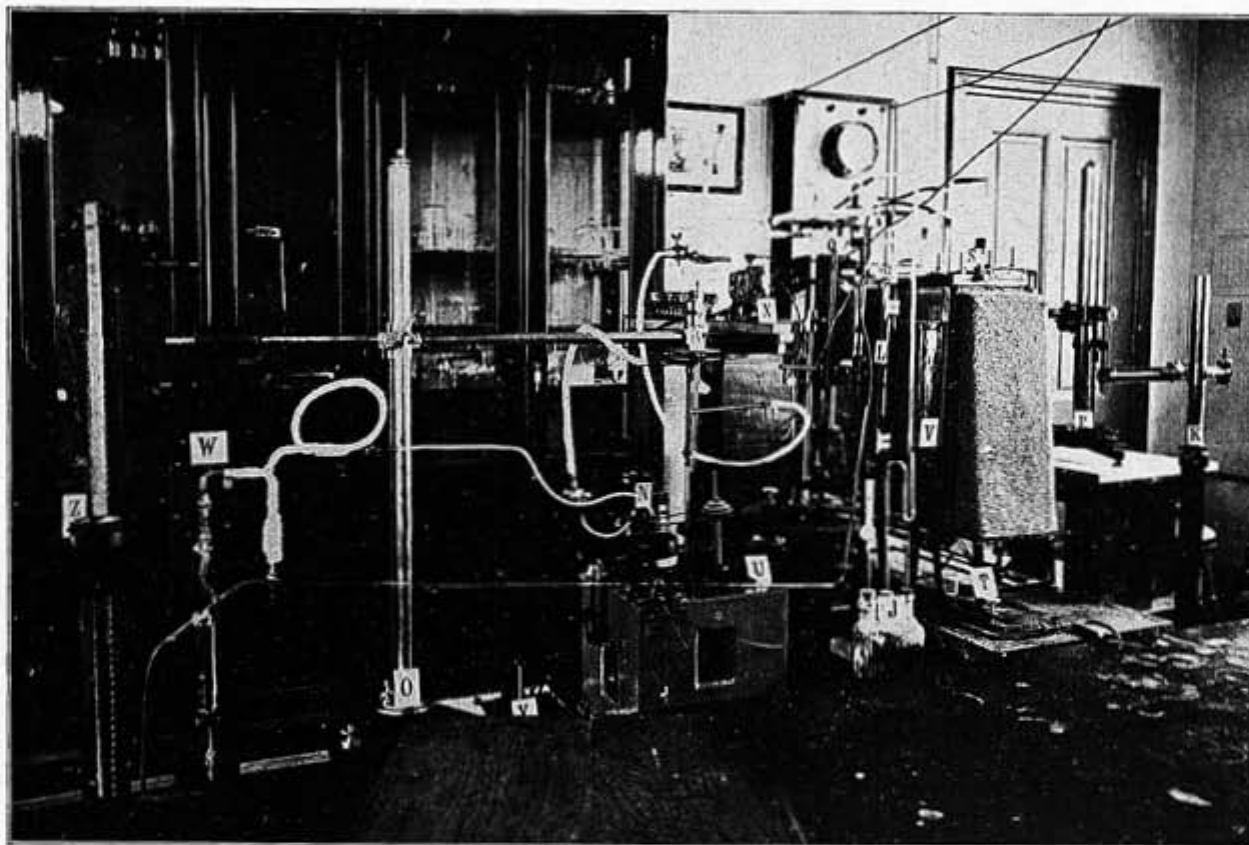
Fig. 6.

§ 20. In the case of POTASSIUMCHLORATE: $KClO_3$, the maximum pressure $H$ was 3,573 mm. mercury at 413°.5 C; at 443°.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:

<div align="center">

At 413°.5 C.    $\chi = 82,4$ Erg. pro cm².

At 443°.5 C.    $\chi = 81,6$ Erg. pro cm².

</div>

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 $\chi$ appeared to *increase* gradually by the generation of $KClO_4$ and $KCl$.

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

With SILVERNITRATE: $AgNO_3$, the value of $\chi$ is about 164 Erg. pro cm². 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.

<div align="center">

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

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**Chemistry.** — *"The Temperature-coëfficients 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 us[1]).

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

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