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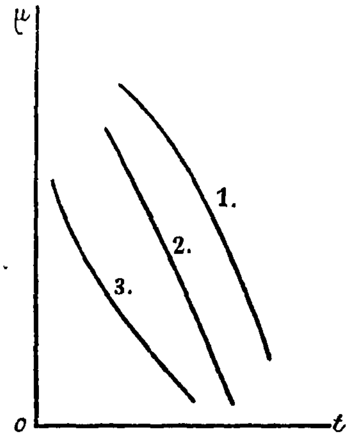
Chemistry. — "*The Temperature-coëfficients of the free Surface-energy of Liquids, at Temperatures from* — 80° *to* 1650°*C*: **VI.** *General Remarks*". By Prof. Dr. F. M. JAEGER. (Communicated by Prof P. ROMBURGH).

§ 1. If we wish to use the results up to now obtained in the study of these more than seventy organic and about ten inorganic liquids, to draw some more general conclusions, the following remarks in this respect may find a place here.

In the first place it is proved once more, that *the free surface-energy of liquids,* — also in the peculiar case of the *electrolytically conducting,* molten salts studied at very high temperatures, — *always decreases with increasing temperature.* This fact, an exception to which also within the temperature-interval hitherto investigated has never been stated, must be esteemed in every respect quite in concordance with the views about the origin of such surface-tensions. It is immediately connected with the other fact, that a *decrease* of the molecular surface-layer must be accompanied by a heat-*evolution,* an *increase* of that layer however with a heat-*absorption,* if the temperature is to remain constant. Furthermore this gradual diminution of χ with increasing temperature is in full agreement with the continual levelling of the differences in properties between the liquid phase and its coexistent vapour, when the temperature is gradually rising: at the critical temperature the value of χ must have become zero[1]).

Of more importance for our purposes however are the following results:

I. A *linear* dependence of χ and t appears in general *not* to exist. The observations prove the possibility of all the three imaginable principal species of χ-t-curves: the type 1, with a concave shape towards the temperature-axis; the type 3 with a shape convex to that axis, and the *rectilinear* type 2. Besides there are found some rare cases of combinations of these three principal types. Characteristic for type N°. 1 is, that $\frac{d\chi}{dt}$ will *increase* with rising temperature, while it *decreases* under those circumstances on the curves of type 3;



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[1]) The critical temperatures of the studied liquids, are as far as known, in the diagrams indicated between ( ), behind the names of the different substances.

only in the case N°. 2 this quotient remains really constant. It is now of importance to draw attention to the fact, *that in contradiction with the hitherto prevailing views, the presence of type 2 on one side, and of types 1 and 3 on the other side, appears to be in no clear connection with the absolute value of the quotient* $\frac{d\mu}{dt}$, *nor with the absolute values of* χ *or* μ *themselves.*

II. In agreement with the results of previous investigators, it appears to be possible, although only in some arbitrary way, to divide the studied liquids into *two* principal groups, with respect to the value of $\frac{d\mu}{dt}$. In the first group A belong all liquids, whose quotients $\frac{d\mu}{dt}$ really are very near to Eötvös' "constant": 2,27 Erg pro every degree Celsius. However it must be said here, that only *a mean value of* $\frac{d\mu}{dt}$ evidently can be considered in these cases, and *only over a sparely extended temperature-interval*; for, just as we already mentioned sub I, these liquids will by no means always show a linear dependence of χ and t, corresponding to the type 2, and therefore such a linear dependence may be supposed in most cases only for rather short parts of the curves in question.

To this group A we can bring e.g.: a number of ethers, like *Ethyl-Isobutyrate* (2,15); *Isobutyl-Isobutyrate* (2,18); *Diethyl-Oxalate* (2,26); *Diethylmalonate* (2,52); *Diethyltartrate* (2,35); *Ethyl-Acetyloacetate* (2,19); further: *Chloroform* (2,06); *Dimethylaniline* (2,23); *Phenetol* (2,14); *Anethol* (2,25); *Methylbenzoate* (2,21); *Ethylbenzoate* (2,29); *Methylsalicylate* (2,30); *Ethylsalicylate* (2,23); *Methylcinnamylate* (2,43); *a-Picoline* (2,02); etc.

With most of these and analogous substances however, we can state a considerable increase of $\frac{d\mu}{dt}$ at *lower* temperatures (type 3), and for many of them a value in the vicinity of 2,27 may be accepted only within a very narrow range of temperatures, e.g. between 25° and 80° C.

To the group B all liquids belong, whose quotients $\frac{d\mu}{dt}$ show values *appreciably lower* than 2,27 Erg pro 1° C. To this group the following substances can be brought: *Water* (1,04); *Ethylalcohol* (0,94); *Propylalcohol* (1,10); *Isobutylalcohol* (1,10); *Acetone* (1,6); *Acetic Acid* (1,3); *Pyridine* (1,6); etc. However with several of these liquids the value of $\frac{d\mu}{dt}$ increases much at the lower temperatures, while to the other side many liquids of group A, which e. g. between 25° and 80° C. show rather normal values of $\frac{\partial\mu}{\partial t}$, will have abnormally low values for it at the higher temperatures. As far as the not numerous determinations of the specific gravities make a conclusion possible in this respect, to this group B can be brought also the molten salts of the alkali-metals: *Sodiumchloride* (0,6), *Potassiumchloride* (0,64); etc. Furthermore the hitherto observed dependence of χ and t for: *Sodiumsulfate, Sodiummolybdate, Sodiumtungstate, Sodiumphosphate*; *Potassiumbromide, Potassiumiodide, Potassiumphosphate, -molybdate, -tungstate*; *Lithiumsulphate, Lithiummetaborate, Lithiummethasilicate*; etc. etc., — seems to prove, that also with these salts the values of $\frac{\partial\mu}{\partial t}$ will appear to be remarkably small.

§ 2. The prevailable opinion is, that the liquids of the group B must differ from those of group A in this respect that they would be *associated*, while the liquids of group A would be *normal* ones. Regarding those liquids, which show an almost linear dependence of χ and t (type 2), the "association-coefficient" x is then calculated from the expression: $x = \left\{\frac{2,2}{\left(\frac{\partial\mu}{\partial t}\right)}\right\}^{\frac{3}{2}}$; while in the cases, where such a linear dependence can *not* be supposed, several other formulae are proposed 1). After what has been said, however, it can hardly be quite sure, that such a calculation of the degree of association can be thought of as a step in the good direction. For among the substances of group A the greater number are of a kind, whose μ-t-curves belong to types 1 or 3; type 3 can be thought moreover again to be in so far in agreement with the postulations of the theory, that here at least exists the possibility that the curve will approach to the t-axis asymptotically in the vicinity of the critical temperature.

If now however the supposition were right, that a decrease of

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1) After VAN DER WAALS (Z. f. phys. **13**. 716. (1894)) e. g., a relation of the form: $\frac{\partial\chi}{\partial t} = A\left(1 - \frac{T}{T_{kr}}\right)^{B}$, — in which B at the critical temperature should have the value: $^3/_2$, but in praxi appears to be: about 1,23, — would reproduce in many cases the dependence of χ and t to a rather sufficient degree.

the values for $\frac{\partial \mu}{\partial t}$ indicated an augmenting degree of association, it would be very difficult to imagine, why the larger number of liquids just show μ-t-curves of the type 3: for from the gradual decrease of $\frac{\partial \mu}{\partial t}$ with increasing temperature in these cases, we must conclude, that the association of the liquid would increase for most liquids with a rise of temperature. But because by far the most dissociations are accompanied by a heat-absorption, the mentioned conclusion could surely be hardly put in concordance with the laws of the mobile equilibrium. With liquids, which will dissociate to a higher degree at higher temperatures, one had to expect on the contrary the progress of type 1: water e.g. is such a liquid, showing a gradual dissociation of complex molecules into simpler ones at increasing temperatures, and the μ-t-curve here really possesses[1] the expected type 1. In the same way we observed some organic liquids (*Diethyl-Oxalate*; *Ethyl-Propylacetyloacetate; Propyl-*, and *Isobutyl-Cyanoacetates*; *o-Toluïdine*; *Resorcine-Monomethylether*; *Hydrochinondimethylether*; *a-Campholenic Acid*; etc.), for which a gradual dissociation or decomposition at higher temperatures could be stated, and for those we found also a faster increase of $\frac{\partial \mu}{\partial t}$ than before, as soon as the temperature of beginning decomposition was surpassed. In opposition therewith is the case of *acetic acid*, where a gradually proceeding depolymerisation with increasing temperature has been quite doubtlessly proved, and where notwithstanding this fact, the value of $\frac{\partial \mu}{\partial t}$ remains constant within very wide limits of temperature.[2]

These facts seem after my opinion to make it very dubious, if the increase or decrease of $\frac{\partial \mu}{\partial t}$ with varying temperature can be esteemed

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[1] From Eötvös' observations one can deduce already immediately that $\frac{\partial \mu}{\partial t}$ will *increase* with rising temperature in the case of *water*: he observes between 3° C. and 40° C. a coefficient: 1,59; between 40° C. and 100° C.: 1,80; between 100° C. and 150° C.: 2,28; and between 150° and 210° C.: 2 27.

[2] Also this fact can be already deduced from Eötvös' observations: between 21° and 107° C he finds for $\frac{\partial \mu}{\partial t}$: 1,32; between 107° and 160° C. also: 1,32; between 160° and 230° C.: 1,38.

any longer to be connected directly with the degree of association of liquids?

§ 3. The variations of $\frac{\partial \mu}{\partial t}$ must in the first instance be dependent on the way, in which the specific heat c of a liquid, is connected with the magnitude S of the bordering layer of it. In general we shall have a relation: $\frac{\partial c}{\partial S} = -T\frac{\partial^2 \chi}{\partial T^2}$, from which follows, that χ can only be a linear function of T in the case, when c is *in*dependent of S. From our measurements however we must doubtlessly conclude, that generally $\frac{\partial^2 \chi}{\partial T^2}$ can not be supposed equal to zero, and that therefore c must really be dependent upon S. This fact proves at the same time, that *the specific heat of the surface-layer must have another value than for the remaining part of the liquid.* The surface-energy therefore cannot be completely of a potential nature, but partially it must be considered as being of kinetic origin. In *what* manner however it will vary with the state of proceeding polymerisation or depolymerisation of the liquid, we cannot tell in advance; and the same is the case *mutatis mutandis* with the dependence of μ upon t.

At the same time it is not superfluous in this connection to fix the attention upon the fact, that it cannot be permitted to make any definitive statement[1]) concerning a high degree of association in the case of molten salts, because the observed values of $\frac{\partial \mu}{\partial t}$ are very small, and the μ-t-curves seem to approach in these cases much better to the rectilinear type **2**. For the whole theoretical exposition of Eötvös cannot be applied to cases like the present one, where nobody can know à priori, if the law of corresponding states will be valid. It is just the *question,* if the measurements still to be made will permit us to draw general conclusions upon an analogous connection between the temperature-coefficients of the molecular surface-energy and the degree of association of such electrolytes? Such conclusions could only be esteemed sufficiently justified, if certain analogies in the behaviour of molten salts and of the organic liquids should be found; at this moment we are still far distant from the time, when we shall be able to give any definitive judgment upon this matter.

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[1]) Vide e. g. the relating views of Walden, Bull. of the Academy of Petrograde loco cit.

§ 4. The rather appreciable differences of our results with respect to the variations of μ and χ with the temperature, with those of other investigators, who have principally worked after the method of capillary ascensions, have suggested to us to investigate in detail, if perhaps in our way of working certain factors could be present, which may cause systematical errors in any direction?

First it was noted, that besides the particular shape of the mentioned curves, also the *absolute* values of χ, determined by us and already by FEUSTEL, were generally somewhat *higher*, than those obtained with the same liquids by other experimenters and by other methods. Of course it is very well possible, that e.g. the lower values published by RAMSAY and SHIELDS, and obtained by them by means of the method of capillary ascension, are caused by the fact, that the moistening of the glass-walls in their capillary tubes has been not so complete, as is supposed in the theory of the phenomenon. In that case the angle of contact φ will play again a role; and because the height of ascension ceteris paribus is proportional to the cosinus of the supplementary angle of φ, there could thus really be found a cause, which would make their results appear *smaller*, than those obtained in our work.

But moreover we were able to prove on the other side, that *our* values for χ, calculated after CANTOR's theory, must surely appear somewhat higher, than they really are, because in praxi the conditions are not completely fulfilled, on which is based the deduction of the *final* formula between H, d_t and r in CANTOR's theory.

Let us start with the somewhat more summary deduction of his formula by FEUSTEL[1]). From this deduction as it is found in the paper of this author, it can be seen, that the formula of CANTOR can have only validity in the special case that the angle θ, which the tangent in every point of the sharp edge of the capillary tube drawn in any azimuth to the rotation-surface of the small gasbubble, makes with the horizontal surface of the liquid, — differs only slightly from 90°; in that case $\theta = 90° - \varepsilon$, wherein ε has a very small value. Some years ago prof. LORENTZ was so kind as to draw my attention to the fact, that this limiting supposition can be avoided, if one makes a few simple substitutions in the two formulae of FEUSTEL:

$$\frac{2\chi}{r} \cos\theta = r \,.\, d_t \,.\, \frac{1}{(1-\cos\theta)^2}$$

and

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[1]) R. FEUSTEL, Ann. d. Phys. loc. cit.

$$H = \frac{r \, . \, d_t \, . \, \sin \theta}{\cos \theta \, (1 - \cos \theta)^2} + \frac{r \, . \, d_t}{3 \sin \theta} \left(\cos \theta + \frac{2}{1 - \cos \theta} \right),$$

by putting: $q = \frac{2\chi}{r^2 \, . \, d_t}$ and $p = \frac{H}{r \, . \, d_t}$, where r is the radius of the capillary tube, and χ and H are the known symbols.

The mentioned formulae can by this substitution be changed into:

$$q = \frac{1}{4 \cos \theta \sin^4 (\theta/_2)} \quad \text{en} \quad p = q \sin \theta + \frac{1}{3} \left\{ \cot \theta + \frac{1}{\sin \theta \sin^2 (\theta/_2)} \right\}.$$

Table of Corresponding Values of θ, q and p

θ	q	p
0°	∞	∞
10	4399,4	793,94
20	292,60	100,080
30	61,717	30,86
40	23,850	15,33
45	16,458	15,21
50	12,192	12,06
55	9 588	9,995
60	8,000	8,660
65	7,098	7,862
70	6,753	7,546
70 31′43″	6,750	7,542
75	7,033	7,814
80	8,433	9,183
85	13,770	14,479
86	16,567	17,269
87	21,277	21,960
88	30,764	31,448
89	59,35	60,027
89°4	63,44	64,12
90	∞	∞

Now it is possible to calculate for a complete series of values of θ, the numbers p and q, and to plot them against each other with respect to rectangular coordinate-axes. If H is measured, and r and d_t are known, p can be calculated for every experiment, and from the diagram the corresponding value of q (and therefore also of χ) can be immediately found. The following table gives a survey of the corresponding values of p and q, for a series of angles θ between 0° and 90° C.

From this table it is seen, that p and q reach simultaneously a *minimum* for $\theta = 70° 31' 43''$, and that Cantor's formula is properly only valid without appreciable error for values of ε between 0° and

0°55'. The corresponding curve generally deviates only a little from a straight line; however we found that this deviation is yet sufficient, to make a correction necessary for all numbers, calculated from CANTOR's formula.

§ 5. From a special case we can now see easily, that the calculation of the results in this way and from CANTOR's formula, *will never cause an appreciable change in the general shape of the* μ-*t*-*curves, and therefore neither in the deduced values of* $\frac{\partial\mu}{dt}$: the deviation of a linear relation between p and q is between $\theta = 70^\circ 31' 43''$ and 90° only so slight, that a somewhat important deformation of the mentioned curves cannot be the result of this difference in computation. However there will be caused *a parallellous shift* of every curve, which will *diminish the absolute values of* χ *and* μ *with a small amount.* That this influence is not at all without importance in the cases hitherto investigated, may be proved in the following way. We choose for this purpose two extreme cases of the here studied liquids: *diethylether,* because the observed values of H are here the smallest, and e.g. a substance as *resorcine-monomethylether,* whose values for H belong to the rather great ones. The calculation is made as follows: H in m.m of mercury (0 C.) is multiplied by the specific weight of mercury, and this number divided by the product $r \,.\, d_t$, (r being expressed in mm.). With the obtained value for p, the corresponding value of q is found from the table or the diagram; this divided by 2 and multiplied by the product $r^2 \,.\, d_t$, gives χ in mG. pro m.m; the number is reduced to Erg pro cm². by multiplication with 9,806.

Diethylether.

t^0	p	q	χ in Erg. cm.$^{-2}$	χ in Erg. cm.$^{-2}$ (CANTOR)	μ in Erg. cm.$^{-2}$	μ in Erg. cm.$^{-2}$ (CANTOR)
—75°	37,53	36,92	28,5	28,9	574,7	582,8
—20°,5	30,60	29,89	21,5	21,9	456,2	464,7
0°	28,28	27,58	19,2	19,6	415,8	424,5
11°	26,93	26,27	17,9	18,4	392,0	402,9
25°	25,61	25,00	16,7	17,1	371,2	380,0
29°,6	25,35	24,70	16,4	16,8	365,9	374,8

The whole χ-t-curve is thus parallellously shifted to an amount of —0,4 Erg.

Resorcine-Monomethylether.

t°	p	q	χ in Erg. cm.$^{-2}$	χ in Erg. cm.$^{-2}$ (CANTOR)	μ in Erg. cm.$^{-2}$	μ in Erg. cm.$^{-2}$ (CANTOR)
— 20°	62,85	62,20	83,1	83,9	1850,1	1867,9
0°	39,89	39,30	51,6	52,4	1161,9	1179,9
46°	34,91	34,30	43,4	44,2	1001,6	1020,1
107°	31,91	31,20	37,5	38,3	896,7	915,8
166°	28,48	27,80	31,5	32,3	782,0	801,8
206°	25,29	24,60	26,8	27,6	682,6	703,0

Here is the χ-t-curve shifted totally to an amount of —0,8 Erg.

This is the correction to be applied, and which was already indicated in our first communication [1]; it has been taken into account since in every case in all the tables. It may here be repeated once more, that although the absolute values of the surface-energy really have approached closer by it to the values formerly published, however the shape of the χ-t-, or μ-t-curves is not altered by it with respect to any particular feature.

§ 6. Another question to be answered with respect to the obtained experimental results, is this, if it may be considered as possible to determine the right values of χ, without being embarrassed therewith by the influence of the *viscosity* of the studied liquid? For just because the internal friction of liquids always increases rapidly at lower temperatures, and an extreme viscosity of the liquid, — even if the bubbling of the gas is executed with extreme slowness, — will cause, as we have seen, the maximum pressure H to appear too great from all kinds of disturbing effects, — the influence of this viscosity could perhaps be advanced as a cause of such a deformation of the χ-t-curves, that they just would manifest a steeper temperature-gradient at the lower temperatures than at the higher. Therewith an explanation of the curves of type 3 would be given; but it must be here remarked already in advance, that such a cause could hardly be adopted for the presence of the curves of type 1, just because all viscosity-curves have themselves the shape of type 3. However there seem to be many reasons, *not* to attribute too high a value to this explanation of the curvature of the μ-t-lines, even not in the case of type 3.

In the first place it must be remarked, that the curvature of the

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[1] F. M. JAEGER, these Proc., Comm. I. (1914).

said curves does not run parallel to the variations of the viscosity with temperature. Most strikingly this can be seen in those substances where the curvature is so slight, that the curves can be considered to be *straight* lines: with *ethylbenzoate,* whose viscosity at 10° is about six times that of acetone, and in a temperature-interval of 50° decreases to two or three times that value, the χ-t-curve is a *straight* line; with the *isobutylbromide,* whose χ-t-curve between 0° and 85° can be considered as a *straight* line, the viscosity decreases to less than half its original value (from 0,008 C.G.S. to 0,003 C.G S.); etc. Neither does the curvature of the χ-t-lines seem to be immediately connected with the absolute value of the viscosity: with *acetic acid,* whose viscosity is about three times, with *salicylic aldehyde,* whose viscosity is four times, with *pyridine,* whose viscosity is about twice, with *phenetol,* where it is circa three times as large as that of ethylalcohol, — in all these cases the curvature of the χ-t-curves is *less* than for the last mentioned liquid, because they are almost straight lines; and with the *aniline* and *nitrobenzene,* whose viscosity is about eight or ten times as great, as that e.g. of the *ethylformiate,* the χ-t-curves are even slightly convex. In many cases the χ-t-curves will show a more rapid and steeper curvature at the higher temperatures, where the viscosity becomes smaller; and the part of the χ-t-curve between — 79° and 0° is often almost a straight line. With the *ethylalcohol* the viscosity is about three times as great as in the case of *ethylacetate* or *ethylformiate,* but notwithstanding that, the χ-t-curves show in all three cases about the same curvature.

To be sure, we have met during our measurements numerous cases, where very clearly the impossibility was shown, to determine the surface-energy *in*dependently of the viscosity. But this we observed only, where the viscosity reached such enormous magnitude, that the liquid became *glassy* or *gelatineous,* and did not or hardly move on reversing the vessel. Such cases we found in: *methyl-cyanoacetate, methyl-methylacetyloacetate, diethylbromomalonate, diethylbenzylethylmalonate*; in undercooled *dimethyl-,* and *diethyltartrate* and *α-campholenic acid,* and very strikingly with *salol* and *resorcine-monomethyl-,* or *dimethylethers.*

Even in these unfavourable cases we succeeded sometimes in making some good measurements; but in most cases this appears to be impossible, which is shown by the fact, that even with so small a velocity of formation of the gas-bubbles as 50 to more than 200 seconds, it proved to be impossible to find a maximum pressure H, which really is *in*dependent of the speed of the nitrogen-flow.

The behaviour of such extremely viscous liquids with respect to the gas-bubbles produced in them, is very variable and often very peculiar: in this case the bubbles are hardly loosened from the capillary tube, in that case one observes a periodic increase and decrease of the gas-pressure, without a bursting of the bubbles occurring; in another case a very large bubble is produced, which suddenly explodes into a great number of very small bubbles; but in no case a maximum pressure can be measured, which is really *in*dependent of the speed of the gas-flow, proving that it corresponds to a real state of equilibrium of the gas-bubble. And this last mentioned fact is so characteristic for all our other measurements: *within rather wide limits one can vary the speed of nitrogen-flow, when working with ordinary liquids, without a measurable change in the determined pressure H being observed.* On the contrary we studied a long series of very *thin* liquids: e.g. *ethylalcohol, diethylether, ethylformiate, ethylchloroformiate, acetone, methylpropylcetone, chloroform,* etc., cooled to —80° C., which notwithstanding the low temperatures gave very reliable values of H, the occasional fact that the temperature is so low, can therefore neither be considered of high importance for the abnormally high values of χ and μ observed. However it must be said in this connection, that Eötvös' relation can no longer be considered as valid at temperatures, lower than about half the absolute critical temperature of the studied liquids.

In this connection it is not superfluous to remark, that with liquids whose volatility is very great, and which therefore possess at higher temperatures a very considerable vapour-tension, there is often some difficulty in obtaining reliable values for H, this maximum-pressure being apparently somewhat increased. However the right value can be deduced in such cases by often repeating the adjustment of the capillary tube, until a really reproducible value will be found. The influence of these abnormally high vapour-tensions cannot be of essential significance, if the measurements are controlled accurately and often carefully repeated.

All arguments taken together, we think it really very improbable, that the changes in viscosity of the studied liquids could be argued as the chief cause of the observed curvature of the χ-t- or μ-t-curves. But in cases of *abnormally great* values of the viscosity, the determination seems doubtlessly no longer possible after this method in any exact way; however with liquids, whose viscosity comes e.g. very near to that of glycerine, or is even somewhat greater, such measurements are already quite reliable if only the formation of the gasbubbles takes place *extremely slowly*: in this way for instance we found again reliable values with: *diethylmalonate* (—20°) and *butyl-*, or *isobutyl-cyanoacetates* (—22°).

Therefore we think it right to draw the conclusion, *that the non-linear dependence of χ on the temperature, must be connected with the very nature of the surface-energy itself, and that it will manifest itself always, as soon the studied temperature-interval is only wide enough.*

We can also mention here the fact, that in the case of molten salts, even at very high temperatures and with very small viscosities of these liquids, we observed just the same three types of χ-t-curves: so with *potassiumiodide* the type 3, with *potassium-metaphosphate* the type 1, with many others the rectilinear type 2, — without it being possible to indicate an immediate reason for it. Finally we can draw the attention to the fact, that notwithstanding the fact that these determinations range over a much smaller temperature-interval, some χ-t-curves of other experimenters (vide e.g. Guye and his collaborators) show, on better consideration, also clearly a deviation from the rectilinear type; for *water* this has moreover already been mentioned before.

§ 7. Finally it is here the place to discuss some points connected with the relations between the magnitude of μ and the *chemical constituents* of the studied liquids, in so far as we may draw conclusions about it already with respect to the sparing experimental data. Moreover the investigations relating to this subject will be continued in this laboratory in a quite systematical way, because a great number of problems have risen in this respect, which only by collecting a more extended experimental material can be answered by generally acceptable views. The facts hitherto gathered are principally adapted, to bring the values of μ in qualitative connection with the *homology* of some analogous compounds, and with the *substitution*-relations between some organic derivatives. This can be executed best by comparison of the μ-t-diagrams, which were published in the successive communications.

A. Homology.

Of *homologous series* we can mention the following:

1. *Ethylalcohol.*
   n.-Propylalcohol.
   Isobutylalcohol.
2. *Ethylformiate.*
   Ethylacetate
3. *Ethylacetate.*
   Amylacetate.

4. *Methylisobutyrate.*
Ethylisobutyrate.
Isobutylisobutyrate.

5. *Acetone.*
Methylpropylketone.

6. *Ethylacetyloacetate.*
Ethylpropyloacetate.

7. *Isobutylcyanoacetate.*
Amylcyanoacetate.
Butylcyanoacetate.
Propylcyanoacetate.
Ethylcyanoacetate
Methylcyanoacetate.

8. *Diethyloxalate.*
Diethylmalonate.

9. *Dimethyltartrate.*
Diethyltartrate.

10. *Trichloromethane.*
Tetrachloromethane.

11. *Benzene*
Toluene.
p-Xylene.
Mesitylene.
Pseudocumene.

12 *Nitrobenzene.*
o-Nitrotoluene.

13. *Aniline.*
o-Toluidine.

14. *Anisol*
Phenetol.

15 *Resorcinemonomethylether.*
Resorcinedimethylether.

16. *Methylbenzoate.*
Ethylbenzoate.
Benzylbenzoate.

17. *Methylsalicylate.*
Ethylsalicylate.
Phenylsalicylate.

18. *Pyridine.*
α-Picoline

By such a comparison of the results obtained we can now derive the evidently general fact, *that the values of the molecular surface energy at the same temperature increase in homologous series, if we come to terms of higher hydrocarbon-radicals.* Although quantitative relations do not so strikingly come to the foreground, it seems however to be clear, that the influence of the same increase in this respect, becomes smaller within the series, if the molecular weight of the compound increases; a fact, that must be thought also completely comprehensible. In most cases these rules hold, as the following instances may prove: The value of μ is at the same temperature greater for *isobutyl-alcohol,* than for normal *propylalcohol,* and here again greater than with *ethylalcohol;* just so with *ethylacetate* greater than with *ethylformiate,* with *amylacetate* greater than with the corresponding *ethyl*ether; it is greater for *isobuthyl-isobutyrate* than for the *ethyl*ether, and here again greater than for *methylisobutyrate;* with *ethyl-propylacetyloacetate* greater than for *ethyl-acetyloacetate.* In the series of the six *cyanoacetates,* the value of μ is greatest with the *amyl*-ether, and decreases here regularly within the series till the *methyl*-ether is reached, while the temperature-coefficients remain almost the same; the *isobutyl*-ether however has another value for $\frac{\partial\mu}{\partial t}$, and values for μ, which are only partially greater than for the *propyl*-ether: in this also a manifestation must be seen of the differences between normal and ramified carbon-chains. In the same way the molecular surface-energy of *diethyltartrate* appears to be greater than of *dimethyltartrate.* In the series of aromatic hydrocarbons, the curves for *pseudocumene* and the isomeric *mesitylene* are situated highest; then follow successively: *p-xylene, toluene,* and *benzene*; in the same μ is greater for *o-toluidine* than for *aniline,* for *o-nitrotoluene* greater than for *nitrobenzene*; just so for *phenetol* greater than for *anisol,* for *dimethylaniline* greater than for *aniline,* and for *α-picoline* greater than for *pyridine.* The only exception to this rule hitherto found, is presented by the *resorcine-monomethylether,* which possesses a greater molecular surface-energy than the corresponding *dimethyl*-ether.

The substitution by means of members of the aromatic series has an analogousinfluence as by those of the aliphatic series, but it is much more intensive: in the series of the *benzoates,* the value of μ for the *ethyl*-ether is indeed, greater than for the *methyl*-derivative. but for the corresponding *benzyl*-ether it is excessively much greater; in the same way it is the case with *methyl-*, and *ethylsalicylates* and *salol,* and with *methylpropylcetone* on one side, and *acetophenone* on the other.

B. Relations of Substitution-derivatives.

The conclusions, which in this respect can be drawn hitherto, can be summed up shortly in the following rules:

1. *The substitution of H by halogens is accompanied by an intensive increase of the molecular surface-energy at the same temperatures; the influence increases evidently with augmenting atomic weight of the halogen.*

So μ for *chlorotoluene* is greater than for *fluorotoluene*[1]), and here much greater than for *toluene* itself, for *bromobenzene* it is greater than for *chlorobenzene,* and appreciably greater than for *benzene*; with the *m-dichlorobenzene* it is greater than for *fluorobromobenzene,* showing that the specific influence of fluorine seems to be less than the difference between bromine and chlorine. In the same way the value for *diethylbromomalonate* is appreciably greater than for *dietylmalonate*; for *tetrachloromethane* just so greater than for *chloroform.*

2. *The substitution of N-atoms for C-atoms, or of that of negative nitrogen containing radicals for a H-atom, is followed by a relatively great increase of the molecular surface-energy at the same temperatures.*

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[1]) The relatively small differences caused by the structural isomerism of these compounds, is here neglected for the present; generally the *para*-substitution seems to be of the highest, the *meta*-substitution of the smallest influence in this respect. We will discuss this peculiarity afterwards by considering the results of a special set of measurements.

So μ is appreciably greater for *o-nitroanisol,* than for *anisol*; for *o-nitrotoluene* much greater than for *toluene*; for *nitrobenzene* much greater than for *benzene*; for *aniline* and *o-toluidine,* much greater than for *benzene* or *toluene.* Just so for *pyridine* appreciably greater than for *benzene*; etc.

3. *The substitution of aromatic hydrocarbon-radicals instead of H-atoms makes the values of the molecular surface-energy also considerably greater.*

So the values for *salol* are much greater than for the other *salicylates*; of *benzylbenzoate* it is much greater than of both the other *benzoates*; of *acetophenone* much greater than of *dimethylcetone* or *methylpropylcetone*; of *diethyl-benzyethylmalonate* much greater than of *diethylmalonate* itself; etc.

Only continued investigations in this direction can however, as has already been said, prove with more certainty, if these rules may be considered as general ones. Researches of this kind will be started in this laboratory within a short time.

Laboratory for Inorganic Chemistry
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Groningen, June 1914.

Mineralogy. — "*On the real Symmetry of Cordierite and Apophyllite*".

By Prof. H. HAGA and Prof. F. M. JAEGER.

§ **1.** In continuation of our investigations¹) on the symmetry of crystals, which can be discerned as mimetic or pseudosymmetrical, we will give in the following a review of the results obtained in our experiments relating to the *cordierite* (*iolite*; *dichroite*) and to the *apophyllite* (*albine*; *ichthyophtalm*). Of both kinds of silicates specimens of *different localities* were at our disposal, — a fact, which hardly can be over-estimated in the study of RÖNTGEN-patterns, as will be proved below. We will describe in the following pages successively our observations with: a) *Cordierite*; b) *Apophyllite.*

§ **2.** *a. Investigations on the true symmetry of Cordierite.*

Cordierite, a silicate of the chemical composition: $H_2(Mg,Fe)_4Al_8Si_{10}O_{37}$, belongs to those minerals, which like the arragonite, imitate the habitus of hexagonal crystals by means of particular polysynthetical twinformations. In literature it is only mentioned, that it is "rhombic"

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¹) H. HAGA and F. M. JAEGER, these Proceedings, XVI. p. 792. (1914).