EUR 165.e

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

DENSITY AND SURFACE-TENSION MEASUREMENTS OF PURE POLYPHENYLS AND SOME POLYPHENYL MIXTURES

by

G. FRIZ and H. VOSSEN

1963

ORGEL Program

Joint Nuclear Research Center
Ispra Establishment - Italy

Heat Transfer Department

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Density is determined by measuring the length of a liquid thread and weight difference. Above the boiling point a sealed capillary is used. Surface tension is measured by the horizontal capillary method with optical observing of the liquid surface at the capillary end. Results are presented for Diphenyl-, Terphenyl-isomers and two industrial mixtures.

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DENSITY AND SURFACE-TENSION MEASUREMENTS OF PURE POLYPHENYLS AND SOME POLYPHENYL MIXTURES

SUMMARY

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Density is determined by measuring the length of a liquid thread and weight difference. Above the boiling point a sealed capillary is used. Surface tension is measured by the horizontal capillary method with optical observing of the liquid surface at the capillary end. Results are presented for Diphenyl-, Terphenyl-isomers and two industrial mixtures.

1. INTRODUCTION

The density of polyphenyls has already been measured several times (R. 1, 2, 3, 4, 5). Mostly the boiling point limited the curves, so that it was desirable to extend the pressure and temperature range. On the other hand the aim was also to measure high boilers, which are difficult to obtain in larger quantities. By reason of this a μ-method was worked out which requests only the small quantity of about 50 mg substance.

The surface tension was measured by BOWRING et al. in 1961 (R. 6) with the vertical capillary method. In Ispra the horizontal capillary-method was taken, for this method too requests only small test portions. The results of the two methods correspond very well.

The measuring program started with pure substances of Diphenyl and of the Terphenyl-isomers and the industrial mixtures OM1 and OM2 from PROGIL. It will be followed by a program for high-boilers.

2. MEASUREMENT OF DENSITY

2.1. Apparatus and procedure of measuring

The density is measured in two steps with a slight difference. In the lower temperature range an open glass capillary (open at one end and closed at the other) is used. It is partly filled with the test liquid. Filling is done with an injection-needle of glass which is heated up together with the test capillary in a special filling furnace, as the polyphenyls are solid at room temperature.

In a glass furnace with an internal aluminium bloc (fig. 4) the test capillary is heated up, and then the length of the liquid thread is measured. After that the difference of weight of filled and empty capillary is determined with a μ-balance. Following a calibrating curve -obtained with water measurements - there is a relation between volume and length of the liquid thread. Weight-difference and volume give density. A little correction must be applied for temperature expansion of the glass capillary. The dimension of the glass capillary are:

material : pyrex
length : 50 mm
outer diameter : 6 mm
inner diameter : 1 mm

The capillary lies in a bore of the aluminium-bloc, which is slitted to allow optical reading of length with a cathetometer by observing the capillary in a 45°-inclined mirror. The furnace is installed horizontally to assure good temperature distribution. The temperature is measured with a thermocouple in a special bore of the bloc. In separate experiments it was verified that capillary-temperature and bloc-temperature correspond within 0,5°C.

The open capillary-method is working up to a temperature of about 30°C below the boiling point. Then begins a markable loss of test portion by vaporisation.

By reasons of this, the range above this temperature is measured with a closed capillary. Half of the capillary is filled with the liquid and then sealed. The first method gave absolute density data below the boiling point. Starting with one of these values, the expansion of the liquid thread allows calculation of density without weighing, provided that the capillary diameter is sufficiently constant over the length. The last condition was tested before.

The method requires some corrections:

1) The temperature-correction for diameter expansion.

2) The vapour-correction which considers the fact that a certain portion of vapour is filling the volume above the liquid thread.
   To calculate this correction, experimental vapour-pressure data and ideal gas law for the vapour were taken.

3) An optical correction for a difference between the reading and the real position of the inner capillary end, by reason of light refraction at the half sphered top of the outer glass surface.
   This correction was calculated, assuming the top to be exactly a half sphere.

In the range below the boiling point the two methods can be compared. The correspondence of the two methods lie within ± 3 %.

2.2. Estimation of accuracy, results.

The accuracy in the absolute (open capillary) method depends on the following: determination of weight-difference and length of liquid thread, temperature measurement and diameter change with temperature. The first and the second error are both in the range of 1 %. The temperature deviation should lie within 2 °C, which results in a maximum error of ± 2 °/oo. The deviations of the calibrating points from a straight line show a scattering of ± 2 °/oo, which are assumed to come from the first two sources of error. The equalized curve is expected to be within this range so that the maximum error is estimated to be in the range of ± 0,5 %.

In the case of closed capillary, the vapour-correction and optical correction are together 1 %. If they are calculated with an error of 20 %, we have an error of 2 °/oo by reason of incorrect calculation. Together with the other effects the maximum error in density will reach 0,5 % too. The comparison of both methods in the range below boiling point shows a deviation from the smoothed curve of less than ± 3 °/oo.

The measuring program started with the pure substances Diphenyl, o-, m-, and p-Terphenyl and the mixtures OM1 and OM2 of PROGIL. The temperature range extended from the point of fusion up to 410-420°C. The results are presented in diagram 1 and 2.

3. MEASUREMENTS OF SURFACE TENSION.

3.1. Apparatus and procedure of measuring.

Figure (5) shows the principle of the apparatus. A capillary is placed in a furnace in horizontal position. It is filled about 20 mm with test liquid. A light-source with parallel beam and a telescope allow optical observation of the flat capillary end. A small pressure pushes the liquid to this end. Without pressure the liquid surface is curved as a half sphere. At a certain pressure this surface is plane. In this moment all the surface reflects the light while at higher or lower pressures only a little spot appears. The effect is very sensitive. The pressure is measured with an instrument which allows reading of 1-2/100 mm H_2O pressure (Miniskop).

The required liquid portions are in the range of 50 mg.

The relation between surface tension and pressure in the case of full wetting liquids is very simple:

$$\sigma = \frac{d}{4} \cdot \Delta p \qquad (d = \text{diameter of capillary})$$

With a certain contact angle α we have the formula:

$$\sigma \cos \alpha = \frac{d}{4} \cdot \Delta p$$

The organic liquid was observed in a free capillary and the contact angle was estimated to be zero, but this is not sufficient for exact measurements. By reason of this additional measurements were done with the bubble-pressure method, which is independent of contact angle. The mean result was: both method correspond within ± 1%. This work will be reported previously.

The capillary is heated up in a furnace with internal bored copper-cylinder. Temperature regulation was done by taking a constant tension source with regulating transformator. The temperature measurement was effected in the same way as in the density apparatus.

The capillary was calibrated with test liquids, so that we have a relative method. Test liquids were: water, benzene, glycerine, formic acid, carbon tetrachloratüm and alcohol. Mean values from 5 tables were taken. They gave a maximum deviation from the best straight line of less than 0,8 %.

3.2. Estimation of accuracy, results.

The scattering of pressure readings at a certain temperature was within the range of ± 3 °/oo. The maximum deviation of the table values from the straight line were 8 °/oo. Other sources of error are: inclination of capillary and change of diameter with length. The first error was suppressed by a careful leveling, taking the liquid thread itself as level indicator. The second source was proved by filling the capillary with different quantities of liquid.

The capillary diameter was found to have sufficient constancy. The temperature deviation should be the same as in the density apparatus, which results in a maximum error of 4 $^{o}/oo$. Considering all these sources of error, we should have an overall maximum error of about 1,5 % for the product

$$\sigma \cdot \cos \alpha$$

Assuming α to be zero, we give in diagram 3 the results of the measurements with Diphenyl and the three Terphenyls. The results are compared with the measuring points of BOWRING (Ref. AEEW-R 41) of 1961, which are obtained with the vertical capillary method.

The diagram contents additionally the curve for a special Hexaphenyl which was obtained within the measuring program of pure highboilers.

LITERATURE

R1	BOWRING R. W. GARTON D. A.	AERE R/R 2762
R2	ANDERSON K.	ANL-5121 (1953)
R3	CORK J. M. et al.	Rev. Sc. Instr. 1(1950) 563
R4	STONE J. P. et al.	Ind. Eng. Chem. 50 (1958)
R5	GERCKE R. H. ASANOVICH G.	NAA-SR-4484
R6	BOWRING RW. et al.	AEEW-R 41

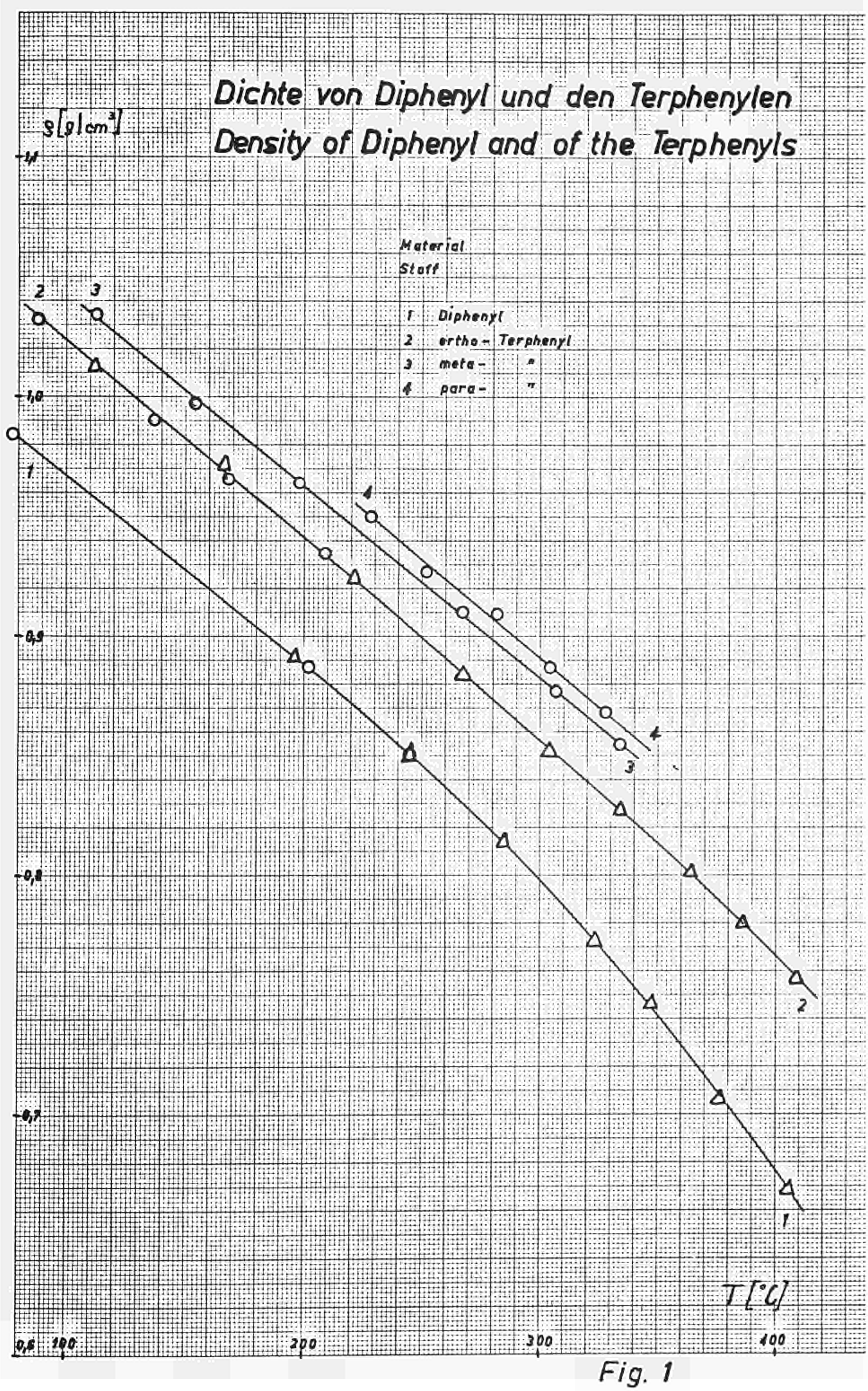
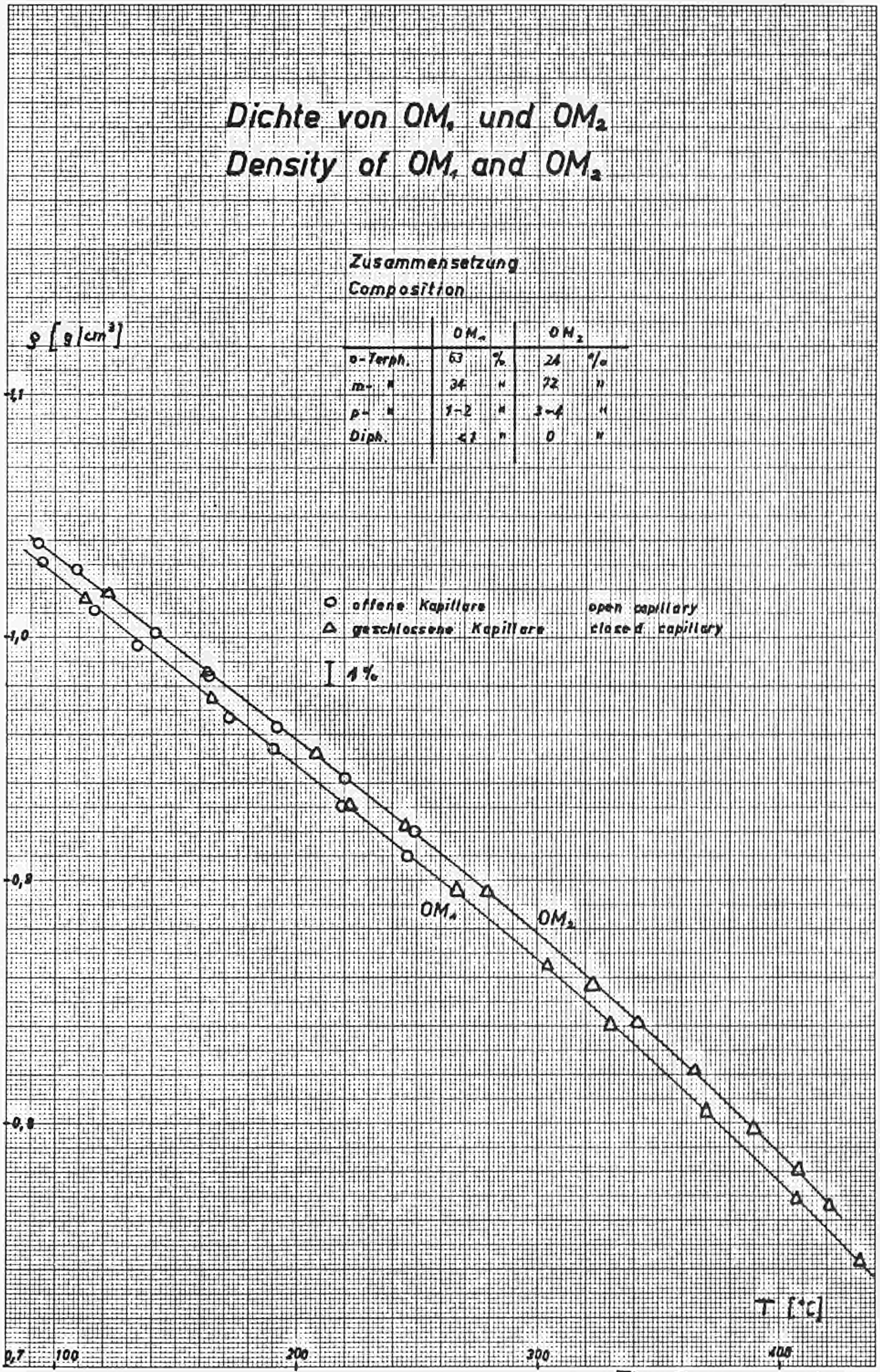

Dichte von Diphenyl und den Terphenylen
Density of Diphenyl and of the Terphenyls
ρ [g/cm³]
1,1
1,0
0,9
0,8
0,7
0,6
100
200
300
400
T [°C]
Material
Stoff
1 Diphenyl
2 ortho - Terphenyl
3 meta - "
4 para - "
1
2
3
4

Fig. 1



Dichte von OM_1 und OM_2
Density of OM_1 and OM_2

Zusammensetzung
Composition

	OM_1		OM_2	
o-Terph.	63	%	24	%
m- "	34	"	72	"
p- "	1-2	"	3-4	"
Diph.	<1	"	0	"

Fig. 2

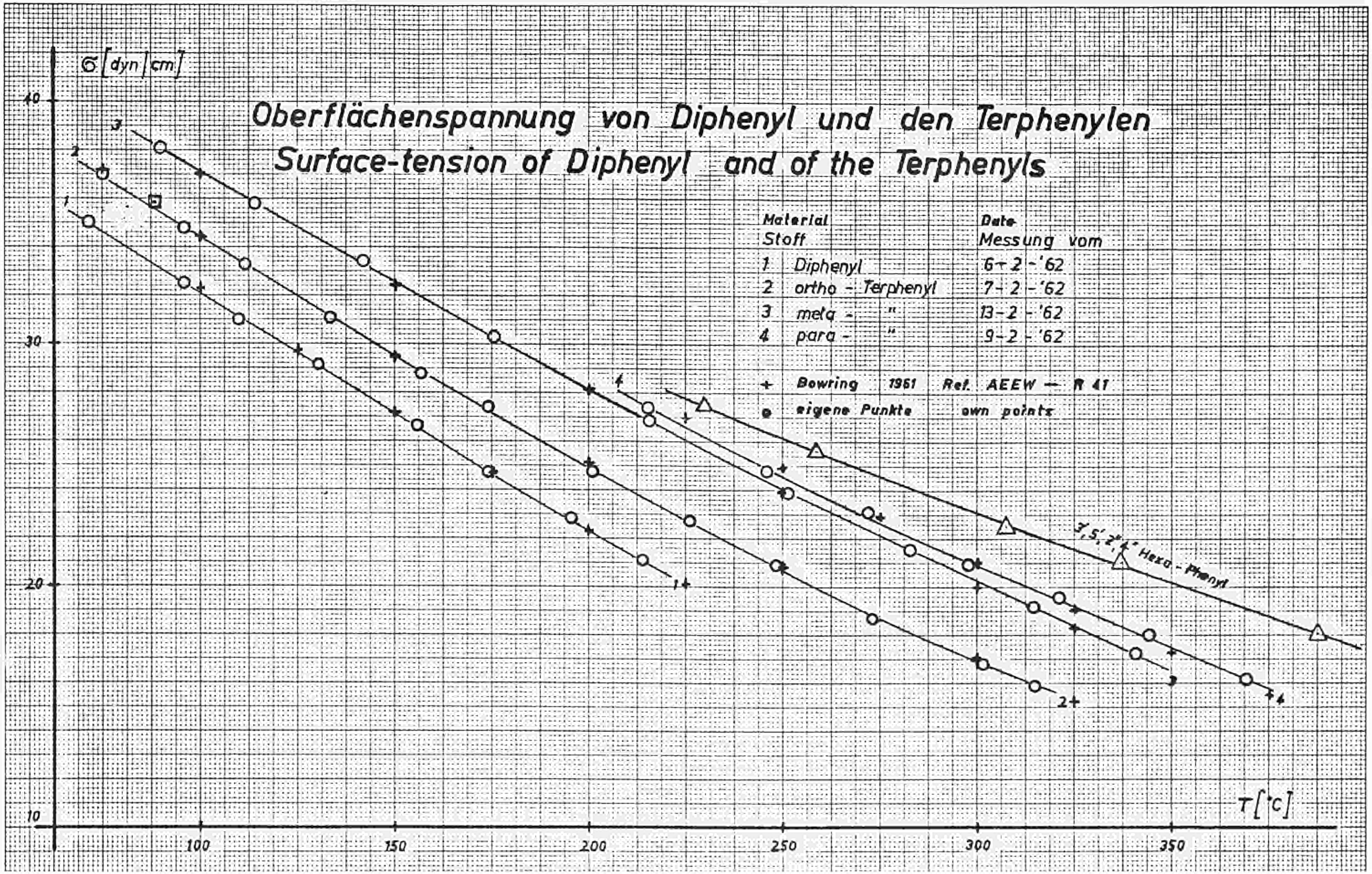

Oberflächenspannung von Diphenyl und den Terphenylen
Surface-tension of Diphenyl and of the Terphenyls
σ [dyn/cm]
40
30
20
10
100
150
200
250
300
350
T [°C]
Material
Stoff
Date
Messung vom
1 Diphenyl 6-2-'62
2 ortho - Terphenyl 7-2-'62
3 meta - " 13-2-'62
4 para - " 9-2-'62
+ Bowring 1961 Ref. AEEW — R 41
○ eigene Punkte own points
1
2
3
4
3,5,2",4" Hexa - Phenyl

Fig. 3

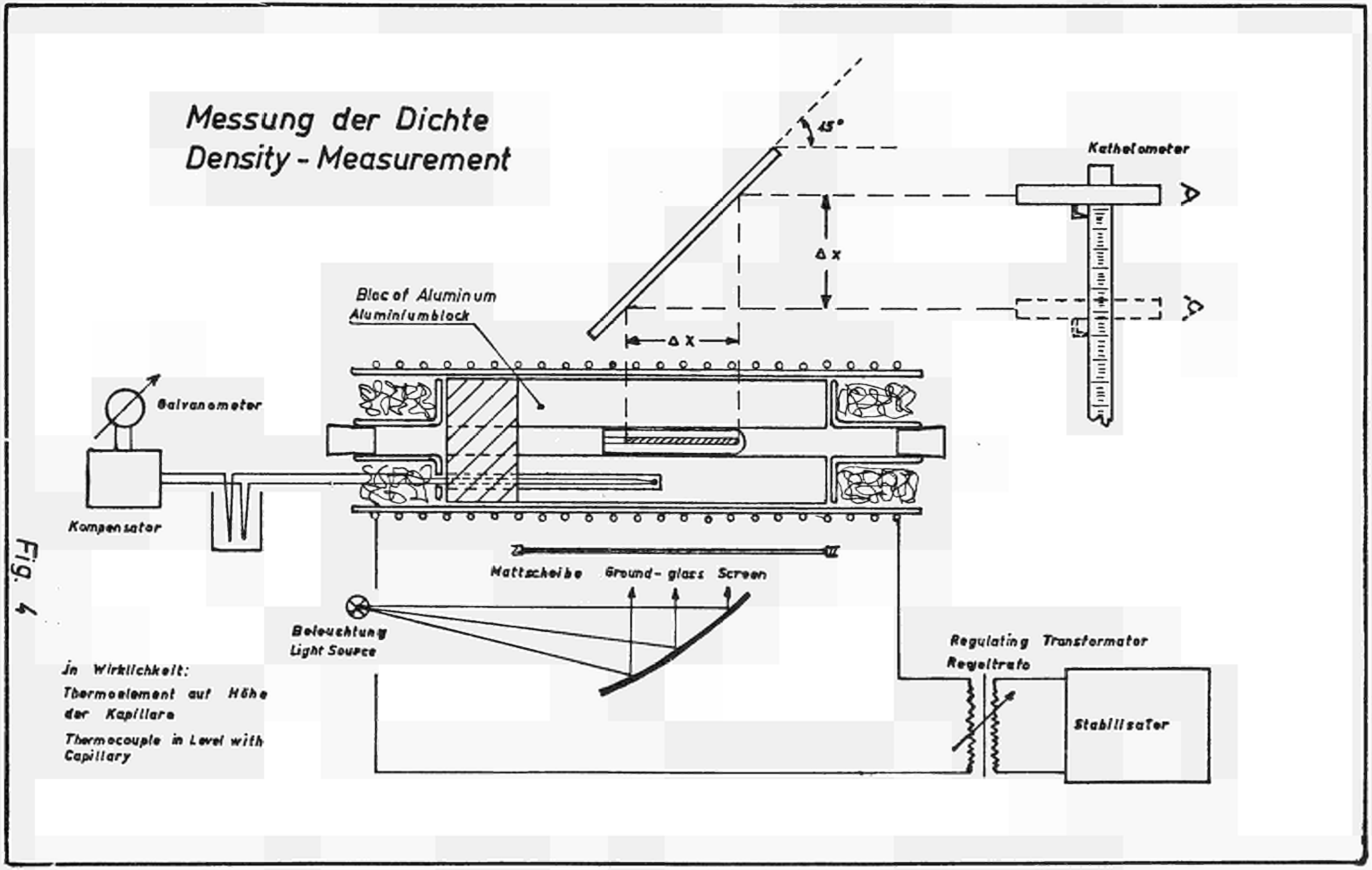
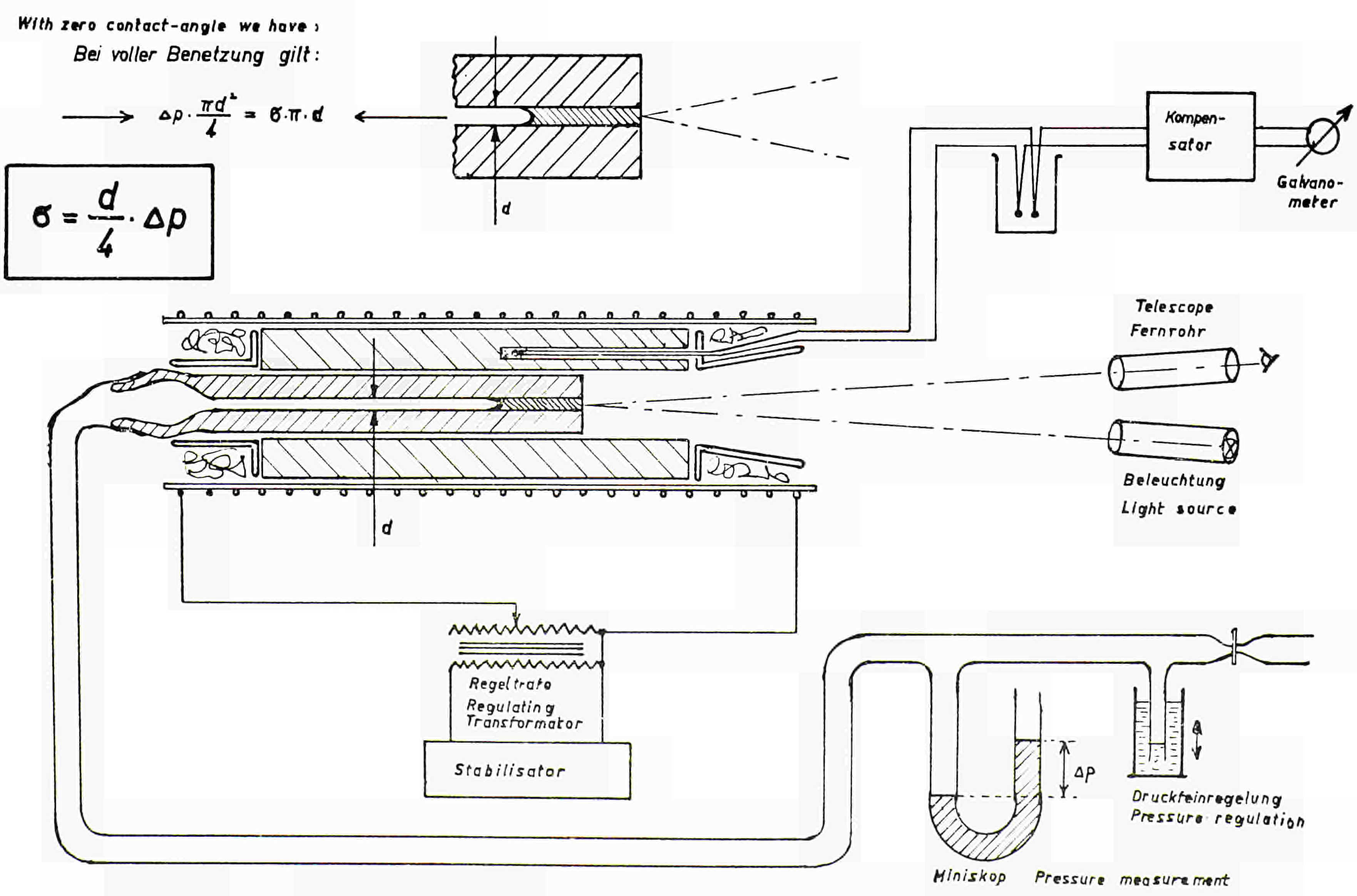


Fig. 4

In Wirklichkeit:
Thermoelement auf Höhe der Kapillare
Thermocouple in Level with Capillary

Fig. 5



Messung der Oberflächenspannung Surface-tension Measurement

CDNA00165ENC