

Report 8975

PHYSICAL-CHEMICAL BEHAVIOR OF  
HYDROCARBONS CONTAINING MORE THAN TWENTY  
CARBON ATOMS

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PHYSICAL-CHEMICAL BEHAVIOR OF HYDROCARBONS  
CONTAINING MORE THAN TWENTY CARBON ATOMS

Dr. W. M. Nazee

SUMMARY

Various synthetic hydrocarbons were prepared, among them, some 2506. saturated with a normal bond and some saturated with a double bond, as well as cyclic. Most of them were produced in the laboratory of Dr. H. J. Backer in Gronigen, several in the laboratory of Dr. J. P. Wibaut in Amsterdam, and several in the laboratory of the "Bataafsche Petroleum Maatschappij".

Much care was employed in the purity of the product at the preparation. Accordingly, the products were subjected to repeated recrystallizations by us. The following constants were determined by us upon a number of these hydrocarbons: melting point, boiling point, refractive index, specific gravity in the liquid and solid states, viscosity, specific heat, heat of transformation, heat of fusion and aniline point.

A number of X-ray photographs were made at our wish of two of the hydrocarbons, normal heneicosane and normal tetracosane, by Dr. J. M. Bijvoet.

Also, the solubilities were determined upon:

n-heneicosane in 2,2,4-trimethylpentane,  
n-tricosane in 2,2,4-trimethylpentane,  
n-tetracosane in acetone, ethanol, chloroform,  
2,2,4-trimethylpentane, and toluene,  
n-hentriacontane in 2,2,4-trimethylpentane.

At the beginning, a study was made of several binary mixtures, namely: n-heneicosane--n-tricosane, n-heneicosane--n-hentriacontane and n-tetracosane--13-methyl-pentacosane. The first case concerns the mixed crystal formation between the components, the two last named cases, a eutetic.

The viscosities of the mixtures of these hydrocarbons were also measured. The measured value was compared afterward with a calculated value of a logarithmic equation and a fluidity equation. The logarithmic equation gave the smallest deviation for the cases investigated.

INTRODUCTION

In this report are included the results of the measurements of 2507 a number of constants of pure hydrocarbons with more than twenty carbon atoms. These measurements were executed in the course of several years time. As is designated in various places, the measurements have not yet been completed. Consequently, uncertain conclusions may be made herein.

Expansion of the measurements either in cases not yet investigated or in cases already investigated, where the correctness of the result is questioned, will be, in this connection, very doubtful values.

FIRST CHAPTER

Method of Preparation of the Hydrocarbons

Since there is described in the literature a method of preparation

for most of the hydrocarbons, produced by us, only those will be mentioned to which have been applied after-treatment by us. A short description of the method of preparation of the remaining hydrocarbons will also be given.

### I. Normal Hydrocarbons

#### n-Heneicosane, $C_{21}H_{44}$ .

The preparation is written in *Rec. Trav. Chim.* 55, 903 (1936). The product was recrystallized five times by us from a very large amount of ethanol and three times from ether. The melting point, determined in a capillary, amounted to 40.3-40.4 C.

#### n-Tricosane, $C_{23}H_{48}$ .

The preparation is likewise included in *Rec. Trav. Chim.* 55, 903 (1936). The product has been recrystallized by us five times from ether and three times from acetone. The melting point amounted to 47.3-47.4 C.

#### n-Tetracosane, $C_{24}H_{50}$ .

Dodecylbromide was prepared from dodecylalcohol, HBr and sulfuric acid. After purification, the substance was dropped into boiling toluene containing sodium. After recrystallization from toluene of the hydrocarbon formed, it was recrystallized eight times from butanone, six times from benzene and five times from ether. The melting point was then 50.7-50.8 C.

#### n-Octacosane, $C_{28}H_{58}$

Tetradecylalcohol was purified by means of acetic acid. This was in return saponified and the alcohol caused to react with HBr and sulfuric acid into the bromide. At this time it was dropped into the boiling toluene in which sodium could be found. After filtering off the NaBr that formed, the preparation was recrystallized first from a mixture of toluene and ethanol and, following that, nine times from ethanol. The melting point was 61.25-61.3 C.

2508

#### n-Triacontane, $C_{30}H_{62}$

A product with a melting point of 66 C was obtained by electrolysis of calcium palmitate. After the recrystallization of the product five times from ether and five times from acetone, the melting point was 65.8-65.95 C.

#### n-Hentriacontane, $C_{31}H_{64}$

This substance was prepared by the heating of calcium palmitate, which in return, had been produced from pure palmitic acid (melting point, 62.3-62.6 C). The palmiton obtained upon distillation of the calcium palmitate was reduced according to the method of Clemmensen. The hydrocarbon was then recrystallized five times from benzene, six times from ether and again five times from benzene. The melting point, 67.2-67.3 C.

**n-Tetratriacontane, C<sub>34</sub>H<sub>70</sub>**

The hydrocarbon is prepared by the electrolysis of calcium stearate. After one recrystallization from ether, the melting point was 72-73 C. Further purification followed in fifteen recrystallizations from ether. Then the melting point was 72.6-72.7 C.

**n-Pentatriacontane, C<sub>35</sub>H<sub>74</sub>**

For the preparation, Rec. Trav. Chim. 59, 933 (1940) can be referred to. The product was recrystallized three times from carbon tetrachloride, whereupon the melting point was 74.4-74.5 C.

**n-Hexatriacontane, C<sub>36</sub>H<sub>74</sub>**

This preparation is described in Rec. Trav. Chim. 59, 933 (1940). After distillation in vacuum and after eighteen recrystallizations, the melting point was 75.8-75.85 C.

**n-Tetracontane, C<sub>40</sub>H<sub>82</sub>**

The preparation of this compound is mentioned in Rec. Trav. Chim. 59, 933 (1940). Another purification was not undertaken by us.

2509

**n-Tritetracontane, C<sub>43</sub>H<sub>88</sub>**

These methods of preparation are also described in Rec. Trav. Chim. 59, 933 (1940). After recrystallization twenty times from carbon tetrachloride, the substance had a melting point of 85.25-85.35 C.

**II. Branched Hydrocarbons****2-Methyltricosane, C<sub>24</sub>H<sub>50</sub>**

This preparation method may be found in Rec. Trav. Chim. 55, 903 (1936). Further purification followed during which the product was recrystallized five times from ether, three times from ethanol, once again from ether, and eight more times from ethanol. The melting point then measured 37.6-37.65 C.

**22-Dimethyldocosane, C<sub>24</sub>H<sub>50</sub>**

The preparation is included in Rec. Trav. Chim. 55, 903 (1936). Finally the preparation was recrystallized four times from ether; thereupon, the melting point amounted to 34.8-34.95 C.

**15-Methylpentacosane, C<sub>26</sub>H<sub>54</sub>**

The complete preparation method is described in Rec. Trav. Chim. 55, 903 (1936). Further purification followed in five recrystallizations from ethanol and five from acetone. Melting point, 22.85-22.95 C.

**10-Nonylnonadecane, C<sub>28</sub>H<sub>58</sub>**

The method of preparation of this substance is also to be found in Rec. Trav. Chim. 55, 903 (1936). It underwent no further methods of purification.

7,12-Dimethyl-9,10-Dihexyloctadecane,  $C_{32}H_{66}$ 

The substance was prepared according to directions of Lerer in "Annual Report of the National Office of Combustible Liquids", 1935, p. 2, in the laboratory of Prof. Wibaut. Octanol-2 was condensed to dicaprylic alcohol (Report 34, 3247). The alcohol was changed to the iodide and treated with sodium and toluene. The hydrocarbon was thereupon obtained. The bright yellow-colored material was dissolved in ether and treated with Morit and Terrana until an odorless, colorless substance was obtained. The freezing point was approximately -78 C. 2510

22-Methyltritetracontane (Methyldiheneicosylmethane),  $C_{44}H_{90}$ 

The method of preparation is described in Rec. Trav. Chim. 59, 933 (1940). After three recrystallizations from carbon tetrachloride, the stable melting point was 66.6-66.7 C. Running the preparation according to the above-named journal, a metastable melting point was at 61.5-62 C.

## III. Cyclic Hydrocarbons

1-Cyclohexyloctadecane,  $C_{24}H_{48}$ 

One may find the preparation method for this hydrocarbon described in Rec. Trav. Chim. 55, 903 (1936).

After the substance had been recrystallized twelve times from acetone, the melting point read 41.5-41.6 C.

1-Cyclohexyl-2-Hexahydrobenzylheptadecane,  $C_{50}H_{98}$ 

This hydrocarbon was prepared according to a journal by Prof. Wibaut and J. Cech (Coll. Trav. Chim. Tsjechoalovaquie (1934) VI, 427).

Palmitic acid was transposed into the ethyl ester. Benzyl chloride was treated with acetic acid, and thereupon was changed with water into a carbinol (1-Phenyl-2-benzylheptadecanol-2). This carbinol was dehydrated and the unsaturated hydrocarbon hydrogenated to 1-Phenyl-2-benzylheptadecane-2.

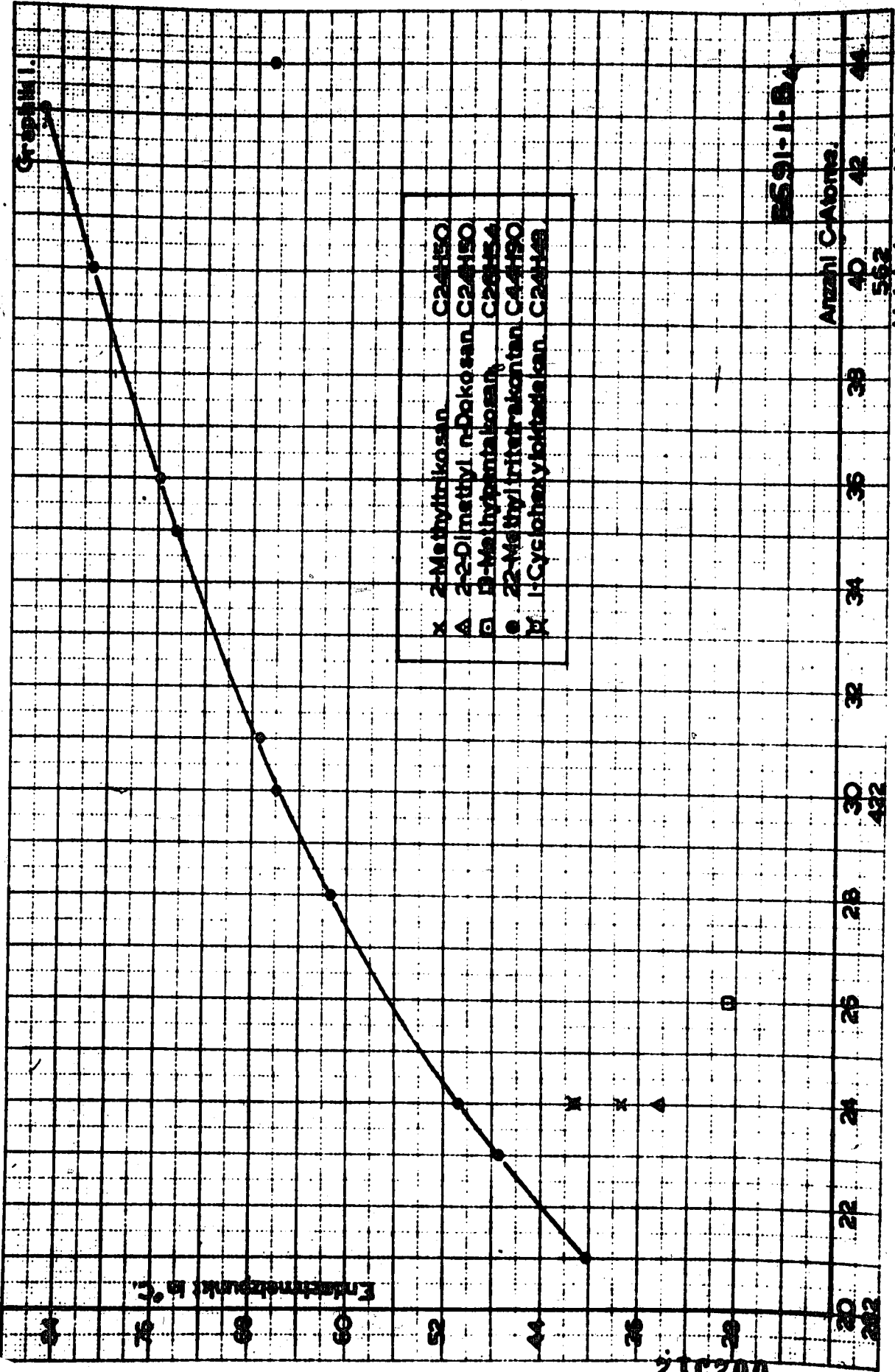
The saturated hydrocarbon, 1-Cyclohexyl-2-hexahydrobenzylheptadecane, has a freezing point of 3.4 C and a melting point of 4.8-7.0 C. The substance was recrystallized by us three times from ether.

## SECOND CHAPTER

I. Determination of the Melting Points and the Boiling Points of Hydrocarbons and the Calculation of the Heat of Evaporation from the Boiling Points at Different Pressures

The melting point of the hydrocarbons was determined by the introduction of a small amount of the pure preparation into a capillary. 2511

Graph III.



- x 2-Methyltridekan C<sub>24</sub>H<sub>50</sub>
- Δ 2-2-Dimethyl n-Dokosan C<sub>24</sub>H<sub>50</sub>
- 2-Methylpentadekan C<sub>26</sub>H<sub>54</sub>
- 22-Methyltridekantan C<sub>24</sub>H<sub>50</sub>
- ⊗ 1-Cyclohexyltridekan C<sub>24</sub>H<sub>50</sub>

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The capillary was then placed against a thermometer reservoir in a beaker containing concentrated sulfuric acid. The sulfuric acid was strongly agitated and at the same time heated very slowly. With a magnifying glass the preparation was observed in the capillary. Indeed, the beginning melting point was noted as well as the ending melting point. The beginning melting point is defined as the temperature at which the first trace of liquid forms in the capillary and the end melting point as the temperature at which the last trace of solid material disappears.

The boiling point was always determined under reduced pressure. Approximately five grams of the preparation was brought to boiling in a specially constructed apparatus under reduced pressure; the steam was condensed in a reflux condenser. If the standardization of the steam temperature had become constant at a determined pressure, this temperature was taken as the right one. It was considered that the temperature determined in this manner was independent of the height of the flame; therefore, the disappearance of boiling was awaited for a correct reading. The boiling point was determined at varying pressures of 1-7 mm. By the equation of Clapeyron:

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2}$$

in which  $p$  represents the steam pressure at the absolute temperature  $T$ , the molecular heat of vaporization (evaporation)  $Q$  may be calculated. In case  $Q$  is not, or is practically not, dependent on the temperature, the  $\log p$  set up against  $1/T$  shall give a straight line, which was the case by the hydrocarbons in the investigated sphere.

The values of the melting points found are summarized in numerical Table I.

Table I

2513

C Atoms	Type	Name of Hydrocarbon	Melting Point, C in the Capillary
	Normal		
21	$C_nH_{2n+2}$	Heneicosane	40.3-40.4
23	"	Tricosane	47.3-47.4
24	"	Tetracosane	50.7-50.8
28	"	Octacosane	61.25-61.3
30	"	triacontane	65.8-65.95
31	"	Hentriacontane	67.2-67.3
34	"	Tetratriacontane	72.6-72.7
35	"	Pentatriacontane	74.4-74.5
36	"	Hexatriacontane	75.8-75.85
40	"	Tetracontane	81.35-81.45 (1)
43	"	Tritetracontane	85.25-85.35
24	Branched	2-Methyltricosane	37.60-37.65
24	$C_2H_{2n+2}$	22-Dimethyl-n-docosane	34.80-34.95
26	"	13-Methylpentacosane	28.85-28.95
28	"	10-Nonylnonadecane	-5 a -6 (2)
32	"	7,12-Dimethyl-9,10-Di-n-hexyloctadecane	ca. -78 (3)
44	"	22-Methyl tritetracontane	66.6-66.7
24	$C_nH_{2n}$	1-Cyclohexyloctadecane	41.5-41.6
30	$C_nH_{2n}$	2 1-Cyclohexyl-2-hexahydrobenzyl-heptadecane	4.8-7.0 (2)

(Continued)

Table I (Continued)

- (1) The preparation is probably not yet entirely pure.
- (2) Not determined in a capillary.
- (3) Freezing point, not determined in a capillary.

The end melting points found are set up in Graph I as a function of the number of carbon atoms, respectively, the molecular weight of the saturated hydrocarbons. As one sees, the melting points of the normal hydrocarbons lie in a flowing curve. The melting point of a branched hydrocarbon always lies lower than the melting point of the normal hydrocarbon with the same number of carbon atoms. The number of the investigated branched hydrocarbons is, however, too small in order to be able to prove a close connection between the melting point and the branching.

In the following table, the values are summarized of the boiling points at various pressures.

2514

Table II $nC_{21}H_{44}$ , Heneicosane

p in mm Hg	log p	t C	T K	1/T
				0.00
1.585	0.200	167.1	440.1	2272
2.02	0.305	172.4	445.4	2245
2.55	0.407	176.6	449.6	2224
3.45	0.538	183.2	456.2	2192
4.31	0.634	187.4	460.4	2172
5.38	0.731	192.6	465.6	2148
6.17	0.790	195.6	468.6	2134

Table III $nC_{23}H_{48}$ , Tricosane

p in mm Hg	log p	t C	T K	1/T
				0.00
2.75	0.440	197.8	470.8	2124
3.52	0.547	203.4	476.4	2099
3.89	0.590	205.5	478.5	2090
5.09	0.707	211.5	484.5	2064
6.13	0.791	215.8	488.5	2046
7.18	0.866	219.4	492.4	2031



Table IV

 $n\text{C}_{24}\text{H}_{50}$ , Tetracosane

p in mm Hg	log p	t C	T K	1/T
				0.00
1.995	0.300	200.0	473.0	2114
3.03	0.462	209.2	482.2	2074
3.43	0.535	212.0	485.0	2062
4.24	0.627	214.2	489.2	2044
4.99	0.698	220.1	493.1	2006
6.49	0.812	225.8	498.8	2005

Table V

 $n\text{C}_{28}\text{H}_{58}$ , Octacosane

2515

p in mm Hg	log p	t C	T K	1/T
				0.00
1.15	0.060	220.8	493.8	2025
1.41	0.150	225.8	498.8	2003
1.76	0.245	230.0	503.0	1988
2.09	0.321	233.6	506.6	1974
2.44	0.388	237.1	510.1	1958
3.44	0.536	245.1	518.1	1928
3.97	0.599	248.3	521.3	1916

Table VI

 $n\text{C}_{30}\text{H}_{62}$ , Triacontane

p in mm Hg	log p	t C	T K	1/T
				0.00
2.08	0.319	250.3	523.3	1911
2.74	0.437	256.7	529.7	1888
3.17	0.501	259.8	532.8	1877
3.88	0.587	264.9	537.9	1859
4.52	0.655	268.7	541.7	1846
5.22	0.718	272.0	545.0	1835
5.81	0.764	274.8	547.8	1826

Table VII

 $n\text{C}_{31}\text{H}_{64}$ , Hentriacontane

p in mm Hg	log p	t C	T K	1/T
				0.00
1.14	0.058	244.6	517.6	1932
1.47	0.167	250.6	523.6	1910
2.28	0.357	260.3	533.3	1875
3.01	0.479	266.7	539.7	1853
3.75	0.572	271.7	544.7	1836
4.52	0.655	275.9	548.9	1822
5.37	0.730	280.1	553.1	1808

Table VIII

 $n\text{C}_{34}\text{H}_{70}$ , Tetratriacontane

2516

p in mm Hg	log p	t C	T K	1/T
				0.00
0.70	0.847-1	253.0	526.0	1902
1.21	0.084	263.9	535.9	1862
1.66	0.221	271.4	544.4	1835
2.11	0.524	276.4	549.4	1820
2.38	0.377	279.35	552.35	1810
2.72	0.434	282.8	555.8	1800
3.13	0.498	285.9	558.9	1786

Table IX

 $n\text{C}_{35}\text{H}_{72}$ , Pentatriacontane

p in mm Hg	log p	t C	T K	1/T
				0.00
1.02	0.010	267.6	540.8	1849
1.75	0.243	279.7	552.7	1809
2.09	0.520	283.7	556.7	1796
2.61	0.417	288.7	561.7	1780
2.85	0.455	290.7	563.7	1774
3.20	0.505	294.0	567.0	1764
3.69	0.567	297.3	570.3	1753

Table X

 $n\text{C}_{36}\text{H}_{74}$ , Hexatriacontane

p in mm Hg	log p	t C	T K	1/T
				0.00
0.67	0.174	265.3	530.3	1858
1.22	0.086	277.4	550.4	1817
1.41	0.149	280.8	553.8	1808
1.60	0.204	284.3	557.5	1794
1.83	0.262	207.3	560.3	1785
2.11	0.324	290.4	563.4	1775
2.59	0.413	294.7	567.7	1762

Table XI

 $n\text{C}_{43}\text{H}_{88}$ , Tritetracontane

2517

p in mm Hg	log p	t C	T K	1/T
				0.00
1.02	0.009	308.0	581.0	1722
1.47	0.167	316.5	589.5	1697
1.89	0.275	321.4	594.4	1682
2.46	0.385	326.4	599.4	1668
2.97	0.473	330.9	603.9	1655
3.55	0.550	336.0	609.0	1642
3.90	0.581	338.5	611.5	1636

Table XII

 $n\text{C}_{24}\text{H}_{50}$ , 2-Methyltricosane

p in mm Hg	log p	t C	T K	1/T
				0.00
2.07	0.317	197.1	470.1	2127
2.79	0.446	203.9	476.9	2097
3.39	0.530	207.3	480.3	2082
4.14	0.617	212.7	485.7	2059
4.82	0.683	215.8	488.8	2046
5.60	0.748	219.1	492.1	2032
7.33	0.865	224.8	497.8	2009

Table XIII $C_{24}H_{50}$ , 2,2-Dimethyldocosane

p in mm Hg	log p	t C	T K	1/T
				0.00
1.28	0.107	183.8	456.8	2189
2.31	0.363	196.4	468.4	2135
3.26	0.513	205.9	478.9	2098
3.69	0.590	207.5	480.5	2081
4.97	0.696	212.9	485.9	2058
6.11	0.786	217.4	490.4	2039
7.03	0.847	221.1	494.1	2024

Table XIV $C_{26}H_{54}$ , 13-Methylpentacosane

2518

p in mm Hg	log p	t C	T K	1/T
				0.00
1.12	0.050	200.3	473.3	2113
1.88	0.275	210.3	483.3	2069
2.94	0.468	219.4	492.4	2031
3.54	0.549	223.0	496.0	2016
4.32	0.635	228.0	501.0	1996
6.18	0.791	235.7	508.7	1966
7.41	0.870	239.8	512.8	1950

Table XV $C_{28}H_{58}$ , 10-Nonylnonadecane

p in mm Hg	log p	t C	T K	1/T
				0.00
1.19	0.075	208.7	481.7	2076
1.69	0.228	216.2	489.2	2044
2.62	0.418	225.3	498.3	2007
3.29	0.517	230.5	503.5	1986
4.47	0.650	237.7	510.7	1958
5.08	0.706	240.5	513.3	1948
5.89	0.770	243.8	516.8	1933

Table XVI

7,12-Dimethyl-9,10-di-n-hexyloctadecane

p in mm Hg	log p	t K	T K	1/T
				0.00
0.83	0.92-1	199.5	472.5	2116
1.09	0.036	204.8	476.6	2093
1.40	0.148	210.9	483.9	2068
1.95	0.290	217.6	490.6	2042
2.27	0.356	220.7	493.7	2027
2.58	0.408	222.6	495.6	2019
2.68	0.429	223.9	496.9	2014
3.20	0.505	227.4	500.4	2000
3.50	0.546	230.0	503.0	1988

Table XVIIC<sub>24</sub>H<sub>48</sub>, 1-Cyclohexyloctadecane

2519

p in mm Hg	log p	t K	T K	1/T
				0.00
1.60	0.203	202.3	475.5	2104
2.16	0.335	208.5	481.5	2077
2.69	0.429	212.9	485.9	2056
3.18	0.502	216.5	489.5	2043
3.91	0.592	221.1	494.1	2024
4.20	0.623	222.5	495.5	2018
5.13	0.710	227.8	500.8	1997
6.71	0.827	234.1	507.1	1972

Table XVIIIC<sub>30</sub>H<sub>58</sub>, 1-Cyclohexyl-2-hexahydrobenzylheptadecane

p in mm Hg	log p	t K	T K	1/T
				0.00
1.92	0.282	244.5	517.5	1932
2.56	0.408	250.9	523.9	1908
2.81	0.449	253.0	526.0	1901
3.19	0.504	255.8	528.8	1890
3.74	0.573	259.5	532.5	1877
3.96	0.598	260.0	533.9	1872
4.50	0.654	263.8	536.9	1852

Table XIX

Hydro- carbon	Name	B.P. in C at 3 mm Hg	Heat of Vaporization		$\frac{d \log p}{d 1/T}$
			in g. cal.		
			Mol.	Spec.	
$nC_{21}H_{44}$	Henicosane	179.8	19450	65.7	4250
$nC_{23}H_{48}$	Tricosane	199.5	20950	64.6	4585
$nC_{24}H_{50}$	Tetracosane	208.6	21550	63.8	4715
$nC_{28}H_{58}$	Octacosane	242.0	22400	56.9	4900
$nC_{30}H_{62}$	triacontane	268.5	23900	56.6	5235
$nC_{32}H_{64}$	hentriacontane	266.2	25100	57.6	5490
$nC_{34}H_{70}$	tetratriacontane	285.4	25800	54.0	5645
$nC_{35}H_{72}$	pentatriacontane	292.3	26650	54.1	5825
$nC_{36}H_{74}$	hexatriacontane	298.4	27450	54.2	6000
$nC_{45}H_{98}$	tritetracontane	332.0	31400	52.0	6870
$C_{24}H_{50}$	2-Methyltricosane	205.0	20950	62.0	4585
$C_{24}H_{50}$	22-Dimethyl-n-docosane	201.5	20500	60.6	4485
$C_{26}H_{54}$	13-Methylpentacosane	219.9	23200	63.4	5070
$C_{28}H_{58}$	10-Nonylnonadecane	228.3	22400	56.8	4910
$C_{52}H_{64}$	7,12-Dimethyl-9,10-di-n-hexyloctadecane	226.0	22700	50.4	4995
$C_{24}H_{48}$	1-Cyclohexyloctadecane	215.3	21400	63.7	4875
$C_{30}H_{58}$	1-Cyclohexyl-2-hexahydrobenzylheptadecane	254.9	23495	56.2	5140

In Graph II the values of  $\log p$  are set up against  $1/T$ . One can see that the points obtained can be combined to make a straight line. The heat of vaporization is thus not dependent on the temperature in the realm investigated. The heats of vaporization, calculated from the slope of the line named, are found summarized in Table XIX. The specific as well as the molecular heats of vaporization are calculated. For comparison of the boiling points of the various hydrocarbons, their values at 3 mm Hg pressure are given in Table XIX, while in Graph III the molecular weight of the saturated hydrocarbons is plotted against the number of carbon atoms, respectively. The boiling points of the normal hydrocarbons make a straight line. The boiling points of the branched hydrocarbons investigated lie with one exception, namely, 1-cyclohexyloctadecane, under the boiling points of the normal hydrocarbons having the same number of carbon atoms.

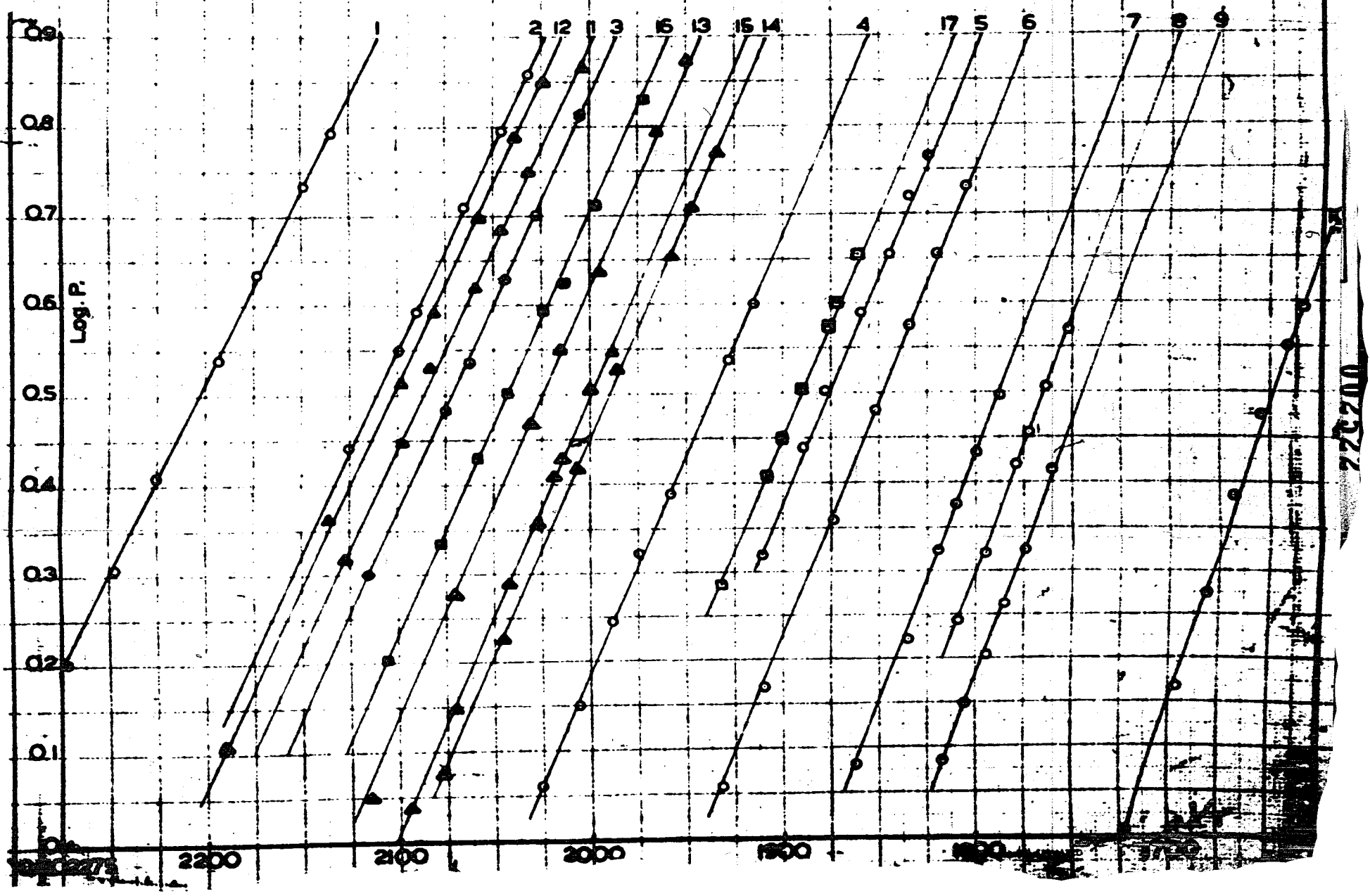
## II. Determination of the Specific Gravities and Refractive Indices of Hydrocarbons in the Liquid State

The specific gravity was determined in a flask with an extended neck and a carefully ground stopper through which a capillary was fitted. 2524 The pycnometer with the melted hydrocarbon was placed in vacuum until no more air escaped.

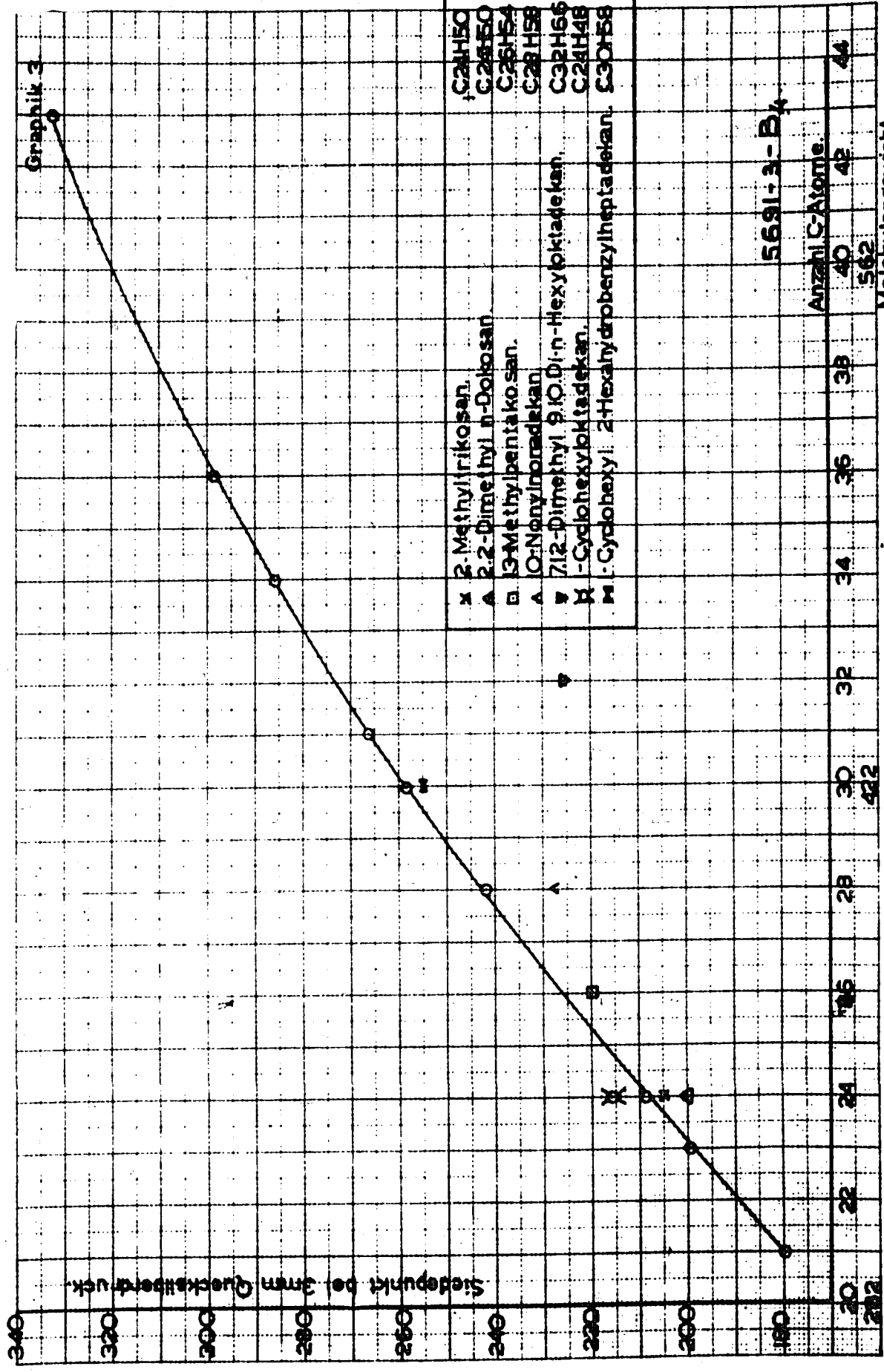
The refractive index was determined in the regular manner, just as the specific gravity, at 70 and 90 C. An Abbe refractometer by Zeiss was used.

Graphik. 2.

1. n- Hendekosan	C 21	H 44
2. n- Trikosan	C 23	H 48
3. n- Tetrakosan.	C 24	H 50
4. n- Oktakosan.	C 28	H 58
5. n- Triakontan.	C 30	H 62
6. n- Hendriakontan	C 31	H 64
7. n- Tetraetriakontan.	C 34	H 70
8. n- Pentatriakontan.	C 35	H 72
9. n- Hexatriakontan.	C 36	H 74
10. n- Tetrakontan.	C 43	H 88
11. 2-Methyltrikosan.	C 24	H 50
12. 2,2-Dimethyl n-Dekosan.	C 24	H 50
13. 13-Methylpentakosan.	C 26	H 54
14. 10-Nonylnonadekan.	C 28	H 58
15. 7,12-Dimethyl 9-iodo, n-Hexyloktadekan	C 32	H 66
16. 1-Cyclohexyloktadekan	C 24	H 48
17. 1-Cyclohexyl-2-Hexahydrobenzylheptadekan	C 30	H 58

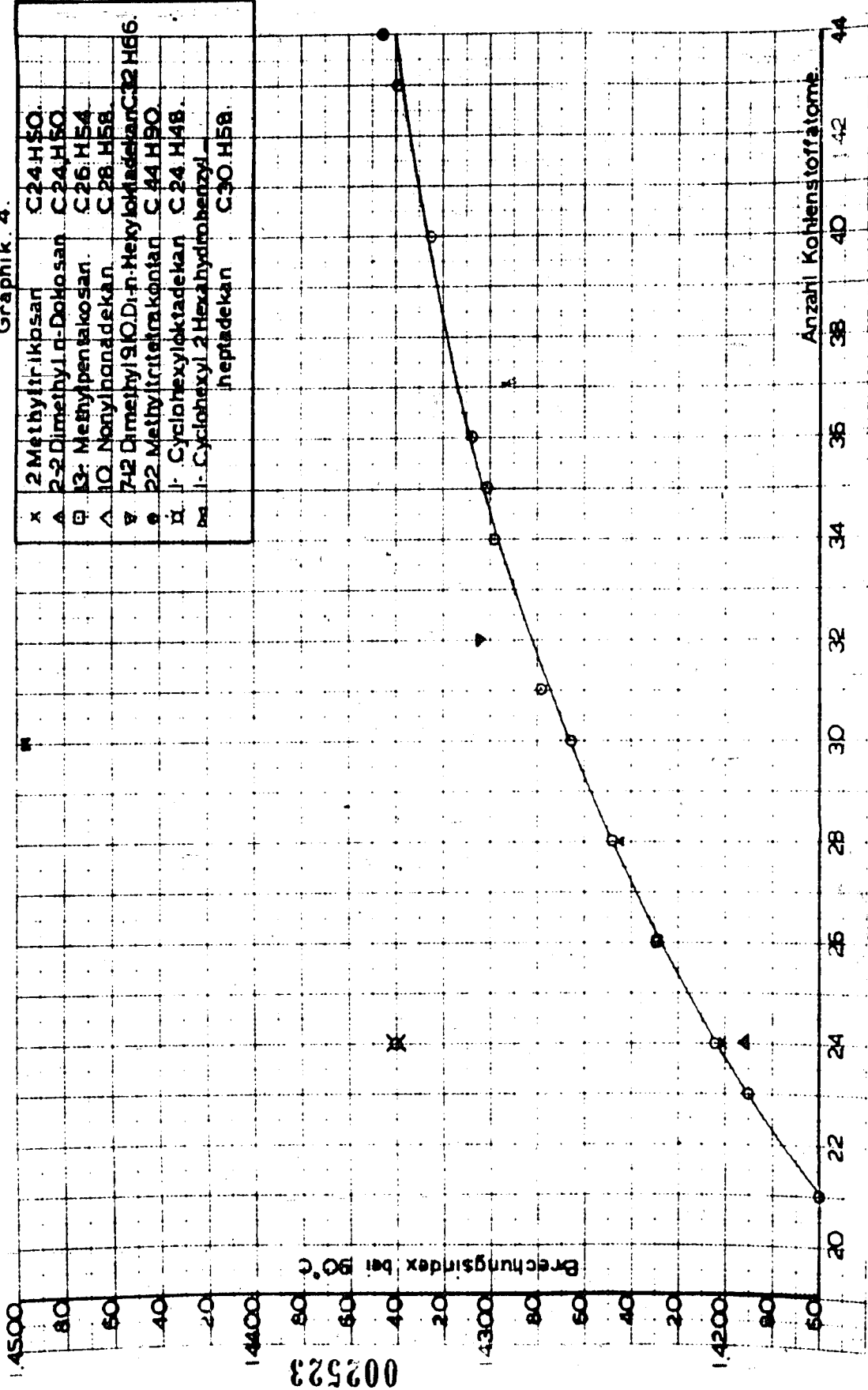


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Graphik. 4.



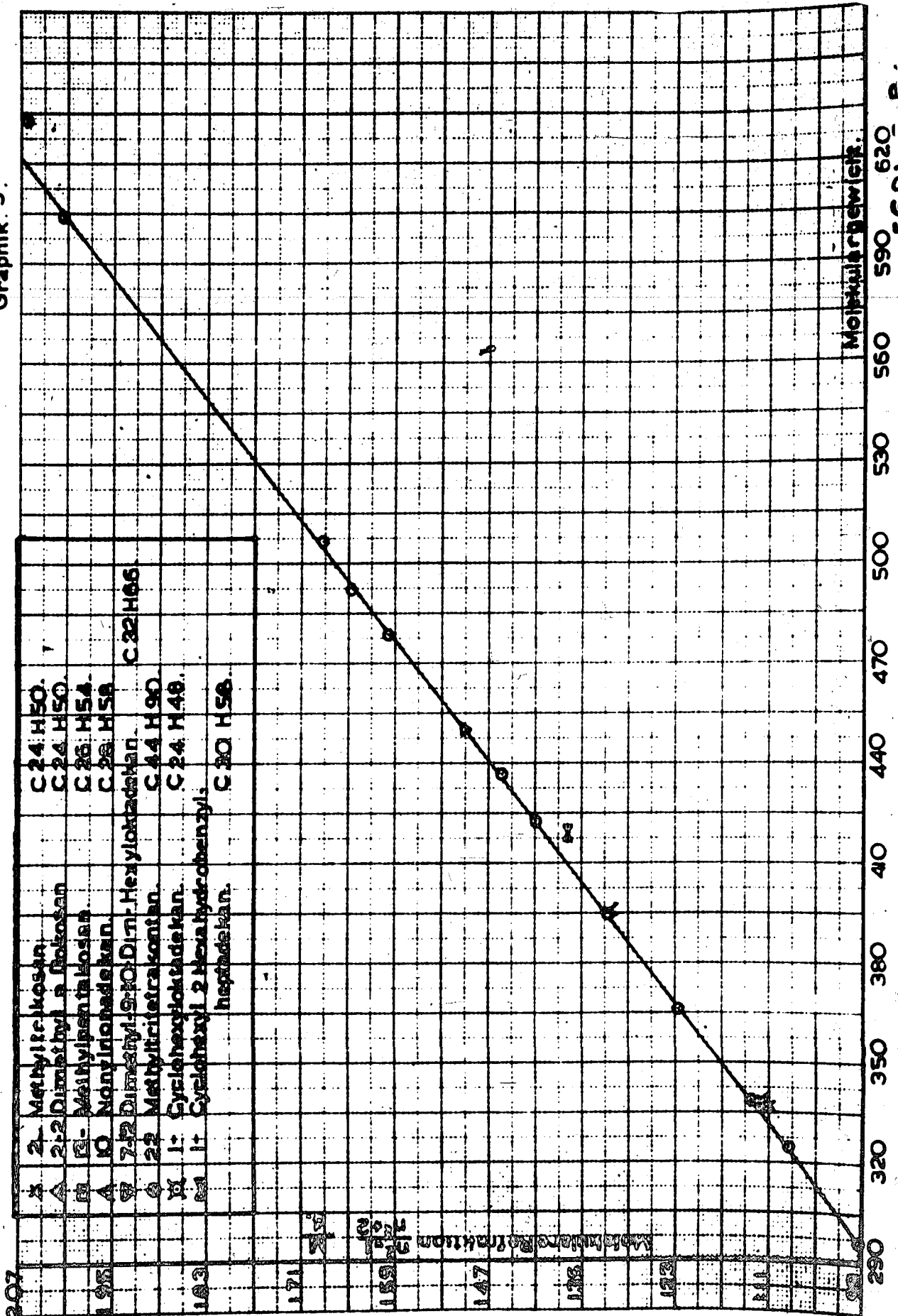
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Table XXI

Number of C atoms	Type	Name	Refractive Index at $n_D^{20}$			Temp. Coeff.	Refractive Index at $n_D^{70}$		
			90 C	70 C	50 C		90 C	70 C	50 C
21	Normal	Heptacosane	1.4160	1.4240	0.00045	99.47	99.58	0.3560	0.3564
25	$C_nH_{2n+2}$	Tricosane	1.4190	1.4270	0.00040	108.64	108.68	0.3553	0.3554
24	"	Tetracosane	1.4205	1.4283	0.00039	113.23	113.23	0.3550	0.3550
28	"	Octacosane	1.4248	1.4324	0.00038	131.82	131.84	0.3546	0.3550
30	"	Triacotane	1.4266	1.4342	0.00038	141.04	141.04	0.3542	0.3542
31	"	Henriacontane	1.4278	1.4354	0.00038	145.45	145.47	0.3536	0.3536
34	"	Tetratriacontane	1.4296	-	-	159.68	-	0.3540	-
35	"	Pentatriacontane	1.4301	-	-	164.37	-	0.3541	-
36	"	Hexatriacontane	1.4306	-	-	168.22	-	0.3525	-
40	"	Tetracontane	1.4320(1)	-	-	-	-	-	-
43	"	Tritetracontane	1.4340	-	-	201.35	-	0.3534	-
24	Branched	2-Methyltricosane	1.4201	1.4276	0.00036	115.48	115.40	0.3557	0.3555
24	"	2,2-Dimethyl-n-docosane	1.4192	1.4269	0.00039	113.51	113.58	0.3552	0.3560
26	"	13-Methylpentacosane	1.4229	1.4303	0.00037	122.68	122.55	0.3552	0.3548
28	"	10-Monylnonadecane	1.4247	1.4322	0.00039	131.60	131.57	0.3540	0.3539
32	"	7,12-Dimethyl-9,10-di-n-hexyloctadecane	1.4305	1.4380	0.00038	149.87	149.70	0.3531	0.3527
44	"	22-Methyltritetracontane	1.4346	1.4417	0.00036	206.17	205.87	0.3536	0.3531
24	$C_nH_{2n}$	1-Cyclohexyloctadecane	1.4359	1.4416	0.00039	111.99	111.08	0.3506	0.3506
30	$C_nH_{2n-2}$	1-Cyclohexyl-2-hexylhydrobenzylloctadecane	1.4495	1.4568	0.00038	136.52	136.49	0.3566	0.3565

(1) Hydrocarbon probably not entirely pure.

Graphik. 5.



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It was noticed that the value of the refractive indices could not be determined so accurately at such high temperatures as at temperatures near room temperature. The inaccuracy amounted to probably 2 or 3 units in the fourth decimal.

In Table XX the values found for the specific gravities at 70 and 90 C are given.

Table XX

Hydrocarbon	Name	Specific Gravity	
		2 70/4	d 90/4
$nC_{21}H_{44}$	Henicosane	0.7587	0.7469
$nC_{23}H_{48}$	Tricosane	0.7654	0.7531
$nC_{24}H_{50}$	Tetracosane	0.7682	0.7562
$nC_{28}H_{58}$	Octacosane	0.7759	0.7639
$nC_{30}H_{62}$	triacontane	0.7795	0.7676
$nC_{31}H_{64}$	hentriacontane	0.7827	0.7709
$nC_{34}H_{70}$	Tetracontane	-	0.7728
$nC_{35}H_{72}$	Pentatriacontane	-	0.7734
$nC_{36}H_{74}$	Hexatriacontane	-	0.7703
$nC_{43}H_{88}$	Tritetracontane	-	0.7612
$C_{24}H_{50}$	2-Methyltricosane	0.7662	0.7539
$C_{24}H_{50}$	2,2-Dimethyl-n-docosane	0.7642	0.7536
$C_{28}H_{54}$	13-Methylpentacosane	0.7720	0.7595
$C_{28}H_{58}$	10-Nonylnonadecane	0.7770	0.7650
$C_{32}H_{66}$	7,12-Dimethyl-9,10-di-n-hexyloctadecane	0.7891	0.7764
$C_{44}H_{90}$	22-Methyltritetracontane	0.7939	0.7816
$C_{24}H_{48}$	1-Cyclohexyloctadecane	0.7997	0.7874
$C_{30}H_{58}$	1-Cyclohexyl-2-hexahydrobenzylheptadecane	0.8334	0.8221

In Table XXI, the values of the refractive indices at 70-90 C are presented. Also the correct values for the molecular and specific refractions of the various hydrocarbons are to be found. In Graph IV the number of carbon atoms is plotted against the refractive indices at 90 C, and in Graph V, the molecular refraction is set up against the molecular weight. In the latter 2527 case, one obtains a straight line for the normal hydrocarbons.

### III. Determination of the Viscosities of Hydrocarbons at Different Temperatures

The viscosity was determined in an Ostwald viscosimeter. Since only a small amount of many of the hydrocarbons remained after their use in other tests, one of the viscosimeters was so constructed that only 5 cc of liquid was needed for the measurement. One of the viscosimeters was adapted to water. One should consider the difference in effective pressure under which the water and hydrocarbon, respectively, flow out in the exact measurement of the viscosity. This difference is slight and will be restricted by the difference between the

surface tension of water and the hydrocarbon. Since no exact measurement is recognized for the surface tension of the melted paraffin, the investigation of the effective pressure for water and for the hydrocarbon had to be made experimentally. For water, this method proved satisfactory; for the hydrocarbon, the investigation remained ineffective for different reasons. This was traced back to the regulation of equilibrium at the measurement of pressure. This was mainly attributed to the fact that at the conditions of measurement of the pressure, the equilibrium standards were obtained very slowly. After several days, this was still not attained. Upon this basis, the effective pressure of water is compared to the hydrocarbon. The viscosity was determined at various excess pressures on about 165, 185 and 210 cm of water, respectively.

The small difference in effective pressures between water and hydrocarbons can be disregarded with respect to excess pressures. Moreover, there is assurance of the conformity between the measurement at these three pressures to the reproducibility of the measurement.

A survey of the values found for the viscosities of the hydrocarbons may be found in Table XXII.

Table XXII

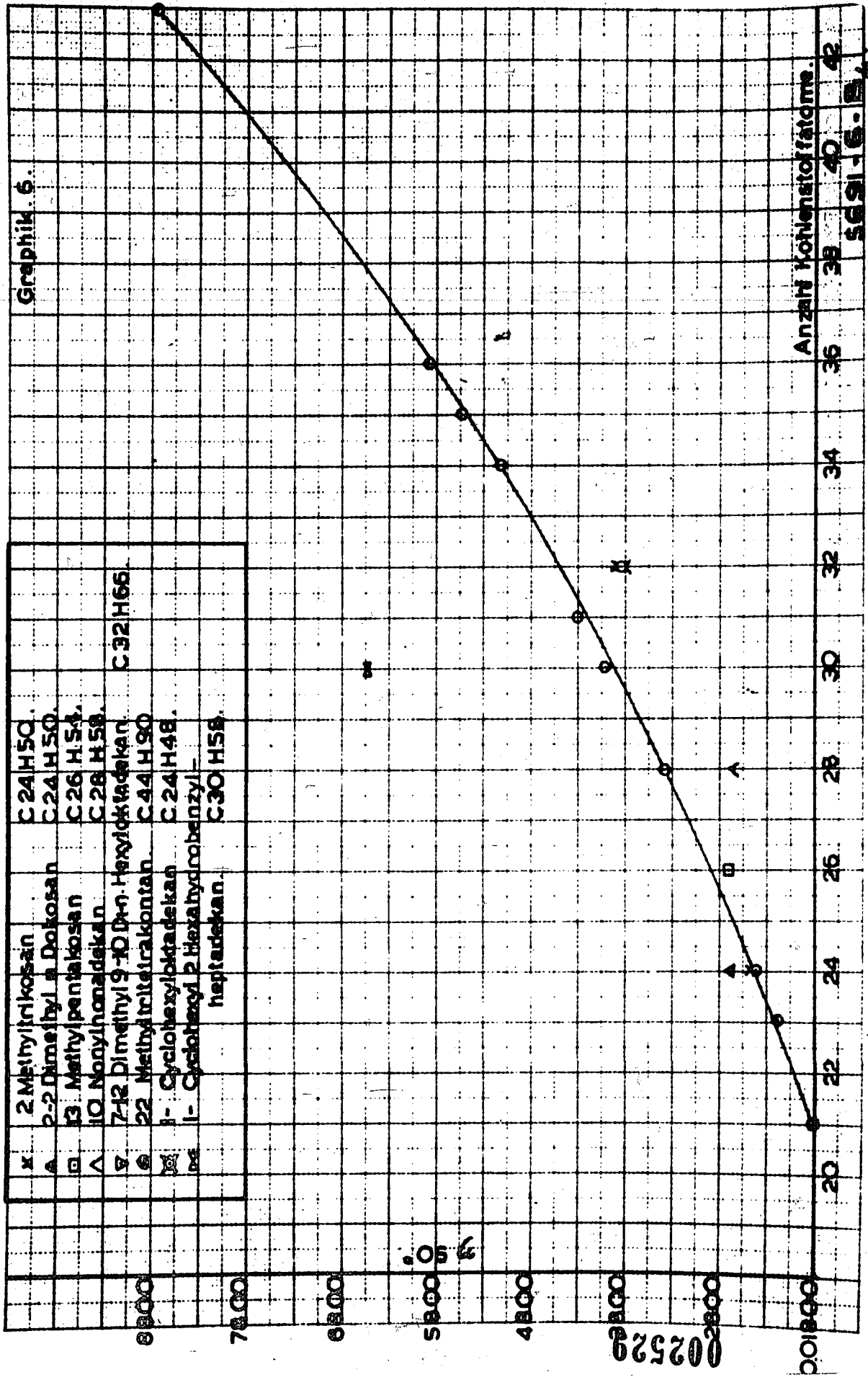
2528

Hydrocarbon	Name	Viscosity		
		90 C	80 C	70 C
$nC_{21}H_{44}$	Henicosane	0.0181	0.0212	0.0252
$nC_{23}H_{48}$	Tricosane	0.0220	0.0261	0.0312
$nC_{24}H_{50}$	Tetracosane	0.0243	0.0288	0.0346 (1)
$nC_{28}H_{58}$	Octacosane	0.0340	0.0410	0.0501
$nC_{30}H_{62}$	triacontane	0.0404	0.0487	0.0604
$nC_{31}H_{64}$	hentriacontane	0.0437	0.0535	0.0660
$nC_{34}H_{70}$	tetratriacontane	0.0514	0.0635	-
$nC_{35}H_{72}$	pentatriacontane	0.0557	0.0683	-
$nC_{36}H_{74}$	hexatriacontane	0.0589(2)	0.0726	-
$nC_{43}H_{88}$	tritetracontane	0.0872	-	-
$C_{24}H_{50}$	2-Methyltricosane	0.0248	0.0295	0.0356
$C_{24}H_{50}$	2,2-Dimethyl-n-docosane	0.0271	0.0326	0.0399
$C_{26}H_{54}$	13-Methylpentacosane	0.0271	0.0324	0.0393
$C_{28}H_{58}$	19-Nonylnonadecane	0.0268	0.0326	0.0403
$C_{32}H_{66}$	7,12-Dimethyl-9,10-di-n-hexyloctadecane	0.0389	0.0492	0.0630
$C_{44}H_{90}$	22-Methyltritetracontane	-	-	-
$C_{24}H_{48}$	1-Cyclohexyloctadecane	0.0318	0.0383	0.0470
$C_{30}H_{58}$	1-Cyclohexyl-2-hexahydrobenzylheptadecane	0.0654	0.0855	0.1149

- (1) By Backer's preparation method.  
 (2) By Backer's preparation method.

The viscosities were determined on several hydrocarbons at still more temperatures than those listed in the table.

Graphik 6.

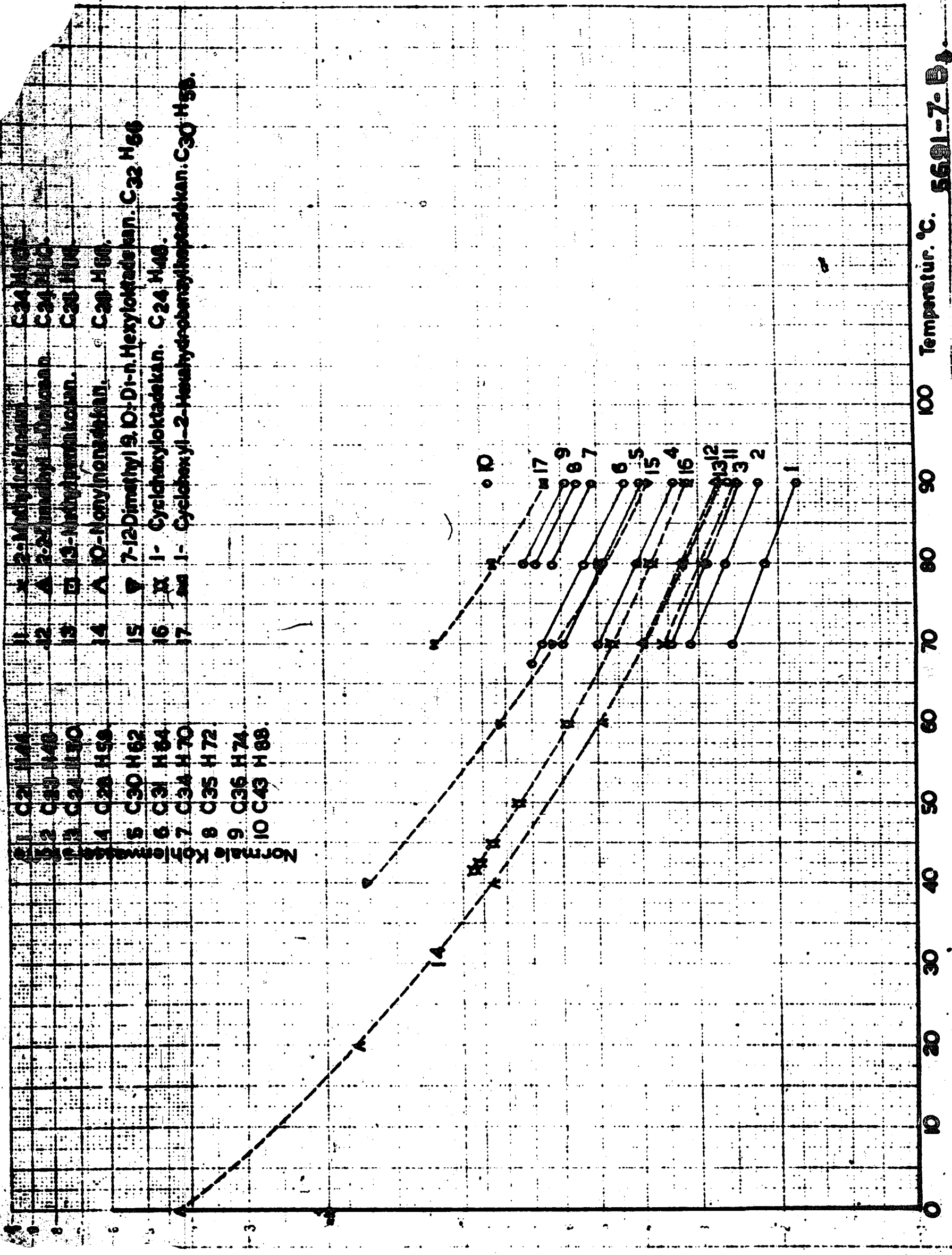


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Graph 7:



n-Hentriacontane, $C_{31}H_{64}$	$\eta_{67}^{\circ}$ , 4 = 0.0704
	$\eta_{67}^{\circ}$ , 5 = 0.0702
10-Nonylnonadecane, $C_{29}H_{58}$	$\eta_{70}^{\circ}$ = 0.4380
	$\eta_{20}^{\circ}$ = 0.1770
	$\eta_{40}^{\circ}$ = 0.0875
	$\eta_{60}^{\circ}$ = 0.0503
7,12-Dimethyl-9,10-di-n-hexyloctadecane, $C_{32}H_{66}$	$\eta_{40}^{\circ}$ = 0.1846
	$\eta_{60}^{\circ}$ = 0.0831
1-Cyclohexyloctadecane, $C_{24}H_{48}$	$\eta_{41}^{\circ}$ , 7 = 0.0956
	$\eta_{42}^{\circ}$ = 0.0947
	$\eta_{42}^{\circ}$ , 5 = 0.0934
	$\eta_{45}^{\circ}$ = 0.0870
	$\eta_{50}^{\circ}$ = 0.0550
	$\eta_{60}^{\circ}$ = 0.0588

In Graph VI, the viscosities of the hydrocarbons at 90 C are set up as a function of the number of carbon atoms. The normal hydrocarbons form a flowing line, while the branched and cyclic sometimes lie above and sometimes below this line. 2531

In Graph VII, the semilogarithmic paper of the  $\log \eta$  is set up against the temperature.

The hydrocarbons hentriacontane and 1-cyclohexyloctadecane are to be observed especially; their viscosities are measured very thickly above the melting point.

The  $\log \eta$ -temperature curves become straight above the melting point, and the course of the curve is normal thereafter. The assumption that the paraffin molecules tend to aggregate above the melting point is not substantiated by the viscosity.

#### IV. Aniline Points of Various Hydrocarbons

The aniline point had already been determined on several hydrocarbons. Enough hydrocarbon and aniline was weighed out in order to have the volume of both substances equal at 90 C. A resume of the values found is given in Table XXIII.

Table XXIII

Hydrocarbon	Name	Aniline Point in C
$nC_{21}H_{44}$	Heneicosane	107.5 C
$nC_{23}H_{48}$	Tricosane	111.4
$nC_{24}H_{50}$	Tetracosane	113.7
$nC_{28}H_{58}$	Octacosane	120.6
$nC_{30}H_{62}$	Triacontane	122.6
$nC_{31}H_{64}$	Hentriacontane	117.2
$nC_{34}H_{70}$	Tetratriacontane	128.8

(Continued)



Table XIII (Continued)

Hydrocarbon	Name	Aniline Point in C
$nC_{35}H_{72}$	Pentatriacontane	130.4
$nC_{36}H_{74}$	Hexatriacontane	129.4
$nC_{45}H_{98}$	Tritetracontane	130.7
$C_{24}H_{50}$	2-Methyltricosane	113.8
$C_{24}H_{50}$	2,2-Dimethyl-n-docosane	115.0
$C_{26}H_{54}$	13-Methylpentacosane	116.0
$C_{44}H_{90}$	22-Methyltritetracontane	139.0
$C_{24}H_{48}$	1-Cyclohexyloctadecane	106.5

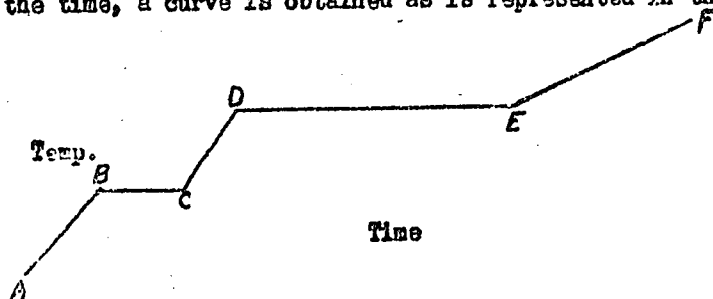
In Graph VIII the number of carbon atoms is plotted as a function of the aniline points. A flowing curve can be drawn through a number of the normal hydrocarbons. Several of the normal hydrocarbons do not lie on this curve, namely,  $n-C_{30}H_{62}$ ,  $n-C_{36}H_{74}$ . The cause of these deviations is not known. Concerning the remaining properties, for example, melting point or refractive index, these hydrocarbons pass in the common rank. Perhaps it should be mentioned here that the concentration by mixing, which has little or practically no influence on the other properties, powerfully affects the aniline point. A closer investigation was desirable regarding this. 2532

Of the branched hydrocarbons, only 2-methyltricosane lies upon the line; 13-methylpentacosane, methyltriheneicosylmethane and 1-cyclohexyloctadecane lie beneath it; and 2,2-dimethyl-n-docosane above the line.

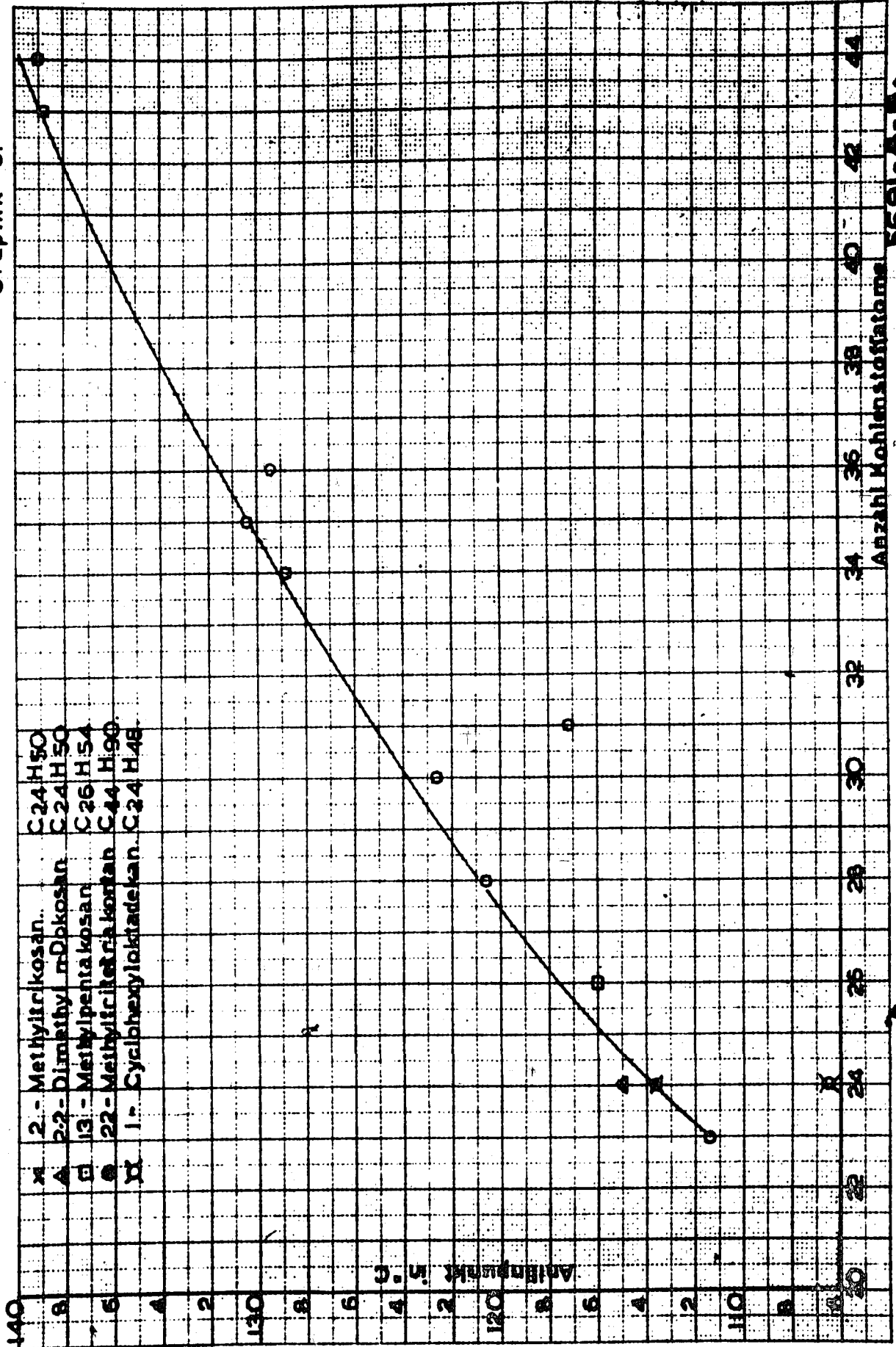
#### V. Determination of the Heat of Fusion, the Heat of Transformation and the Specific Heat of Hydrocarbons

The following method was employed for the determination of the hydrocarbons named in thermal volume.

A. The temperature will rise by the addition of heat until the melting point or a transition point is reached. The temperature will remain constant as long as the melting point or transformation reaction is in motion, but it will again rise as soon as this is completed. If the temperature is set up against the time, a curve is obtained as is represented in the following drawing.



Graphik 8.



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AB introduces the solid substance in the first modification; BC, the transformation of the first into the second modification; CD, the warming curve of the second modification; DE, the melting process; and EF, the warming curve of the liquid.

If the addition of heat per unit of time is known, then the length of the curves, the specific heat, the heat of transformation and the heat of fusion of the substances can be calculated from the slope. 2534

#### B. Detailed Explanation of the Method.

A cylindrical, silver vessel with a diameter of about 1.8 cm and a height of about 2 cm contains thickly compressed, gold-plated nickel gauze. In the middle of the vessel is found a room for the reservoir of a thermometer.

The vessel was placed in a flask which itself is located in a water bath. The temperature difference between the vessel and the thermostat was held at a constant value during the entire experiment. Usually around 10 C was chosen. By gaging with naphthalene, the number of calories that had been added to the vessel per minute at various temperatures could be known. Since the principal of these methods (detailed by Straub and Malotaux) has been described in literature, only a brief description is included here. Several corrections were introduced by us in everything.

Determination of the thermal volume with the help of a calorimeter made possible the exact results that have been given. Nevertheless, the first method was favored, and this because the apparatus is cheap and simple and because the values can be obtained with more ease in an hour's time. Moreover, the possibility of the observations of this method is effective over greater temperature changes.

The inferior accuracy of several per cents that were obtained by this method, favored for the purpose designated, namely, obtaining an insight into the behavior of the paraffin hydrocarbons, verifies the disadvantages of the time-consuming calorimetric method.

The determination of the quantities was carried out, in case the preparation was pure as possible, in duplicate, most of the time even in triple or quadruple.

The average values for the heat of transformation, in so far as these hydrocarbons possess a transition point, and for the total melting heat may be found in Table XXIV.

It should be noted that the heat of transformation is very high in comparison to the melting point. It can be seen that the total melting heats, thus, the melting point at the lowest temperature where the normal hydrocarbons are of stable modification, deviate little from one another. 2535

Table XXIV

Hydrocarbon	Name	Heat of Transformation		Total Melting Heat	
		in cal./g.	at	in cal./g.	at
C <sub>21</sub> H <sub>44</sub>	Heptacosane	12.3	32.8	57.1	40.4
C <sub>23</sub> H <sub>48</sub>	Tricosane	16.6	40.6	59.8	47.4
C <sub>24</sub> H <sub>50</sub>	Tetracosane	21.0	47.4	60.8	50.8 (1)
	"	21.1	46.6	60.3	50.8 (2)
C <sub>28</sub> H <sub>58</sub>	Octacosane	15.4	54.2	57.7	61.3
C <sub>30</sub> H <sub>62</sub>	triacontane	14.4	59.2	56.7	65.9
C <sub>31</sub> H <sub>64</sub>	hentriacontane	15.4	61.8	57.7	67.3
C <sub>34</sub> H <sub>70</sub>	tetratriacontane	-	-	-	-
C <sub>35</sub> H <sub>72</sub>	pentatriacontane	14.9	71.6	57.5	74.5
C <sub>38</sub> H <sub>74</sub>	hexatriacontane	14.2	73.5	55.6	75.8 (1)
	"	14.1	73.4	-	- (2)
C <sub>40</sub> H <sub>82</sub>	tetracontane	-	-	56.0	81.5
C <sub>43</sub> H <sub>88</sub>	tritetracontane	-	-	56.8	85.4
C <sub>24</sub> H <sub>50</sub>	2-Methyltricosane	-	-	48.8	37.7
C <sub>24</sub> H <sub>50</sub>	2,2-Dimethyl-n-docosane	-	-	47.0	35.0
C <sub>26</sub> H <sub>54</sub>	13-Methylpentacosane	-	-	46.7	29.0
C <sub>28</sub> H <sub>58</sub>	10-Nonylnonadecane	-	-	-	-
C <sub>44</sub> H <sub>90</sub>	Methyldiheneicosylmethane	-	-	-	-
C <sub>28</sub> H <sub>58</sub>	1-Cyclohexyloctadecane	-	-	52.3	41.5

- (1) Prepared by Prof. Backer.  
 (2) Prepared by Prof. Wibaut.  
 (3) Probably the product is not very pure.

The specific heat of the various hydrocarbons was determined at various temperature limits, depending on the experimental conditions. The values found for the various hydrocarbons as an average of at least two experiments are given in Table XXV.

Table XXV.

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nC <sub>21</sub> H <sub>44</sub>			nC <sub>25</sub> H <sub>48</sub>			nC <sub>24</sub> H <sub>50</sub>			nC <sub>28</sub> H <sub>58</sub>		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
15-21	0.45	S <sub>2</sub>	25-35	0.47	S <sub>2</sub>	25-35	0.43	S <sub>2</sub>	25-35	0.43	S <sub>2</sub>
21-32	0.47	S <sub>2</sub>	43-47	1.12		35-45	0.48	S <sub>2</sub>	35-45	0.54	S <sub>2</sub>
24-39	1.36	S <sub>1</sub>	55-65	0.60	S <sub>1</sub>	45-50	0.97	S <sub>1</sub>	45-53	0.63	S <sub>2</sub>
45-55	0.57	L			L	52-61	0.58	L	54-60	1.01	S <sub>1</sub>
									62-75	0.61	L

(Continued)

Table XXV (Continued)

$n\text{C}_{30}\text{H}_{62}$			$n\text{C}_{31}\text{H}_{64}$			$n\text{C}_{35}\text{H}_{72}$			$n\text{C}_{36}\text{H}_{74}$		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
25-55	0.47	S <sub>2</sub>	25-35	0.46	S <sub>2</sub>	25-35	0.44	S <sub>2</sub>	25-35	0.45(1)	
										0.41(2)	S <sub>2</sub>
										0.50	
55-45	0.52	S <sub>2</sub>	35-45	0.50	S <sub>2</sub>	35-45	0.50	S <sub>2</sub>	35-45	0.46	S <sub>2</sub>
										0.56	
45-57	0.60	S <sub>2</sub>	45-55	0.58	S <sub>2</sub>	45-55	0.54	S <sub>2</sub>	45-55	0.55	S <sub>2</sub>
										0.76	
60-65	0.98	S <sub>1</sub>	63-66	1.04	S <sub>1</sub>	55-65	0.65	S <sub>2</sub>	55-65	0.72	S <sub>2</sub>
										0.93	
67-77	0.61	L	75-85	0.60	L	65-70	0.83	S <sub>2</sub>	65-72	0.89	S <sub>2</sub>
										1.08	
						72.5-73.5	1.15	S <sub>1</sub>	74-75	1.36	S <sub>1</sub>
										0.61	
						75-80	0.65	L	77-86	0.61	L

$n\text{C}_{40}\text{H}_{82}$			$n\text{C}_{43}\text{H}_{88}$		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
30-40	0.41	S	43-50	0.50	S
40-50	0.45	S	50-60	0.56	S
50-60	0.53	S	60-70	0.62	S
60-70	0.80	S	70-76	0.74	S
70-80	0.96	S	76-83	0.92	S
82-90	0.60	L	86-91	0.63	L

- (1) Prepared by Prof. Backer.  
(2) Prepared by Prof. Wibaut.

$n\text{C}_{24}\text{H}_{50}$			$\text{C}_{24}\text{H}_{50}$			$\text{C}_{26}\text{H}_{54}$			$\text{C}_{24}\text{H}_{48}$		
2-Methyltricosane			2,2-Dimethyldocosane			13-Methylpentacosane			1-Cyclohexyloctadecane		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
13-23	0.44	S	15-25	0.47	S	15-25	0.43	S	15-25	0.43	
33-43	0.55	L	25-33	0.48	S	35-45	0.55	L	25-35	0.42	
			37-45	0.55	L				45-55	0.57	

Table XXVI

$nC_{21}H_{44}$			$nC_{25}H_{48}$			$nC_{24}H_{50}$			$nC_{28}H_{58}$		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
15-21	0.45	S <sub>2</sub>	25-35	0.47	S <sub>2</sub>	25-35	0.43	S <sub>2</sub>	25-35	0.48	S <sub>2</sub>
21-32	0.47	S <sub>2</sub>	43-47	1.12		35-45	0.48	S <sub>2</sub>	35-45	0.54	S <sub>2</sub>
34-59	1.98	S <sub>1</sub>	55-65	0.60	S <sub>1</sub>	45-50	0.97	S <sub>1</sub>	45-55	0.63	S <sub>2</sub>
45-55	0.57	L			L	52-61	0.56	L	54-60	1.01	S <sub>1</sub>
									62-75	0.61	L

$nC_{30}H_{62}$			$nC_{31}H_{64}$			$nC_{35}H_{72}$			$nC_{38}H_{74}$		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
25-35	0.47	S <sub>2</sub>	25-35	0.46	S <sub>2</sub>	25-35	0.44	S <sub>2</sub>	25-35	0.45(1)	
									25-35	0.41(2)	S <sub>2</sub>
										0.50	
35-45	0.52	S <sub>2</sub>	35-45	0.50	S <sub>2</sub>	35-45	0.50	S <sub>2</sub>	35-45	0.46	S <sub>2</sub>
										0.56	
45-57	0.60	S <sub>2</sub>	45-55	0.58	S <sub>2</sub>	45-55	0.54	S <sub>2</sub>	45-55	0.55	S <sub>2</sub>
										0.76	
60-65	0.98	S <sub>1</sub>	63-66	1.04	S <sub>1</sub>	55-65	0.65	S <sub>2</sub>	55-65	0.72	S <sub>2</sub>
										0.93	
67-77	0.61	L	75-85	0.60	L	65-70	0.83	S <sub>2</sub>	65-72	0.89	S <sub>2</sub>
										1.08	
						72.5-73.5	1.13	S <sub>1</sub>	74-75	1.36	S <sub>1</sub>
										0.61	
						75-80	0.63	L	77-86	0.61	L

$nC_{40}H_{82}$			$nC_{45}H_{88}$		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
30-40	0.41	S	43-50	0.50	S
40-50	0.45	S	50-60	0.58	S
50-60	0.53	S	60-70	0.62	S
60-70	0.80	S	70-76	0.74	S
70-80	0.93	S	76-83	0.92	S
82-90	0.80	L	86-91	0.65	L

$C_{24}H_{50}$			$C_{24}H_{50}$			$C_{26}H_{54}$			$C_{24}H_{48}$		
Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat		Temp. Range	Spec. Heat	
2-Methyltricosane			2,2-Dimethyltricosane			13-Methylpentacosane			1-Cyclohexyloctadecane		
13-23	0.44	S	15-25	0.47	S	15-25	0.43	S	15-25	0.45	
39-48	0.55	L	25-33	0.48	S	35-45	0.55	L	25-35	0.42	
			37-45	0.55	L				45-55	0.57	

(1) Prepared by Prof. Backer.  
(2) Prepared by Prof. Wibaut.

All normal hydrocarbons investigated containing from 21 to 36 2537 carbon atoms, had a transition point which ranged several degrees below the melting point. This contradicted the observations of A. Müller (1), who found no transition point for n-C<sub>21</sub>H<sub>44</sub> and C<sub>23</sub>H<sub>46</sub> but a varying of structure up to the melting point. It is probable that Müller's product was not entirely pure. The branched hydrocarbons listed in Table XXIV possess no stable transition points for the temperatures investigated. For 22-methyltritetracontane, Backer and Strating (2) found a metastable melting point.

Worth noting is the strong dependence of the specific heat of hydrocarbons on the temperature. The high specific heat is astonishing; these behaved somewhat similarly to the density under the stable modification of normal paraffins to the melting point. The specific heat of the normal hydrocarbons which have no transition point, namely, C<sub>40</sub>H<sub>82</sub> and C<sub>48</sub>H<sub>98</sub> are also high under the melting point; they reached a value that lies between 0.9 and 1.0.

#### VI. Properties of Hydrocarbons in the Solid State

At our wish, under the direction of Dr. J. H. Bijvoet in the Laboratory of Crystallography at the University of Amsterdam, two of the hydrocarbons, heneicosane (C<sub>21</sub>H<sub>44</sub>) and n-tetracosane (C<sub>24</sub>H<sub>50</sub>), were subjected to several X-ray analyses at varying temperatures.

It can be supposed that it is possible by X-ray analysis to exactly determine the cells of the lattice of a crystal. The transition point is marked by a sudden change of these measurements so that in the revolution apparatus of hydrocarbon density under the melting point, one can say that the cell measurements correspond. However, a pycnometer-determined density changes in an analogous manner. The measurement of length of a rhombic cell has more decomposition than the simple measurement of volume, and of course not only because the cell formation comes into light at approximately the same cell volume, but because the change in form of the cell crystals gives an indication of the type of structure change.

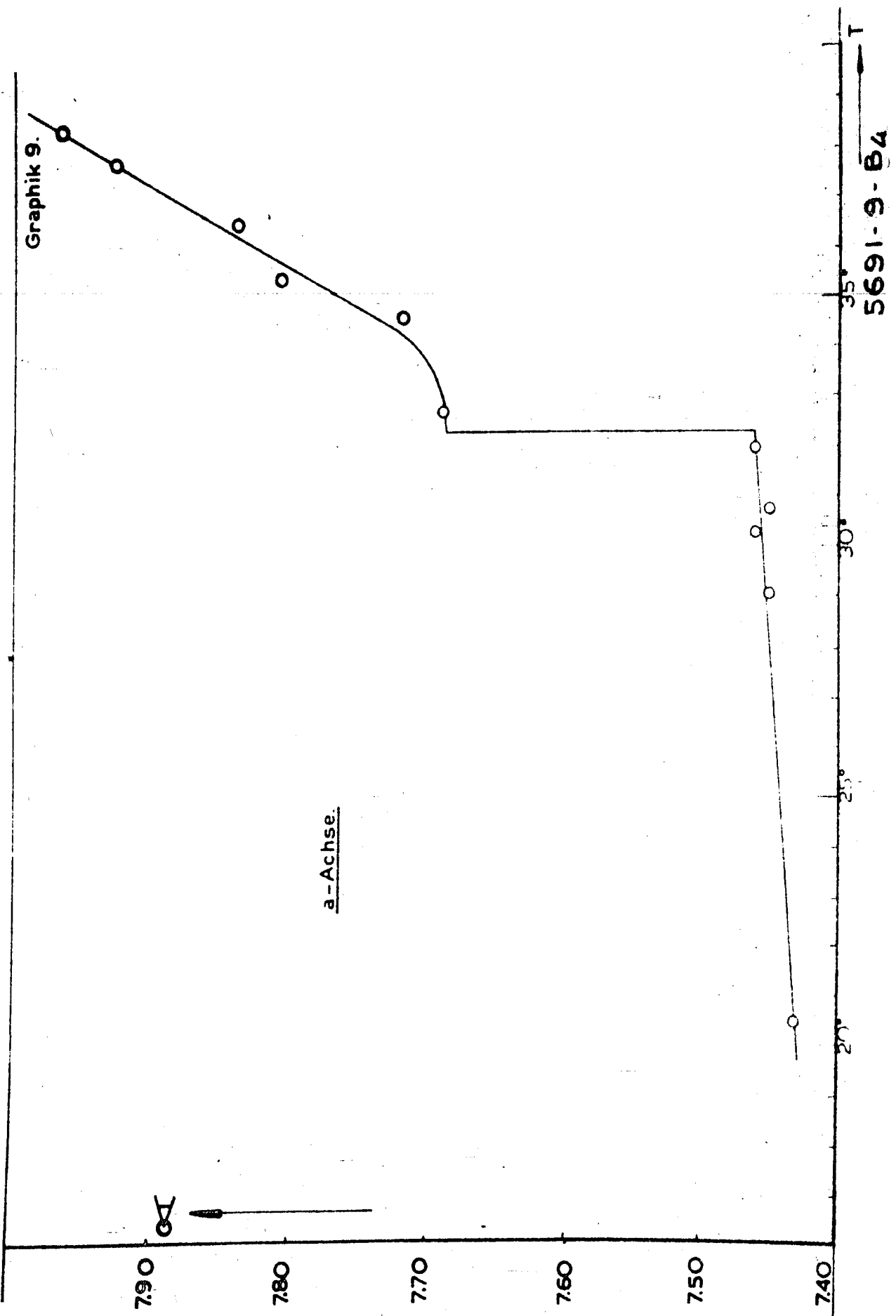
A survey was made of n-C<sub>21</sub>H<sub>44</sub> at the following temperatures 2542  
(in Centigrade): 20.5, 29.1, 30.5, 30.8, 32.0, 32.7, 33.7, 34.6, 35.3, 36.4, 37.6, 39.3.

The length of the a- and b-axis was measured each time at these temperatures. The values for the a-axis, b-axis, 100 x 1/ab and a/b are given in Table XVI.

(1) Proc. Royal Soc. London A. 120, 437 (1938); A. 120, 437 (1938).

(2) Rec. Trav. Chim. LIX, 942 (1940).

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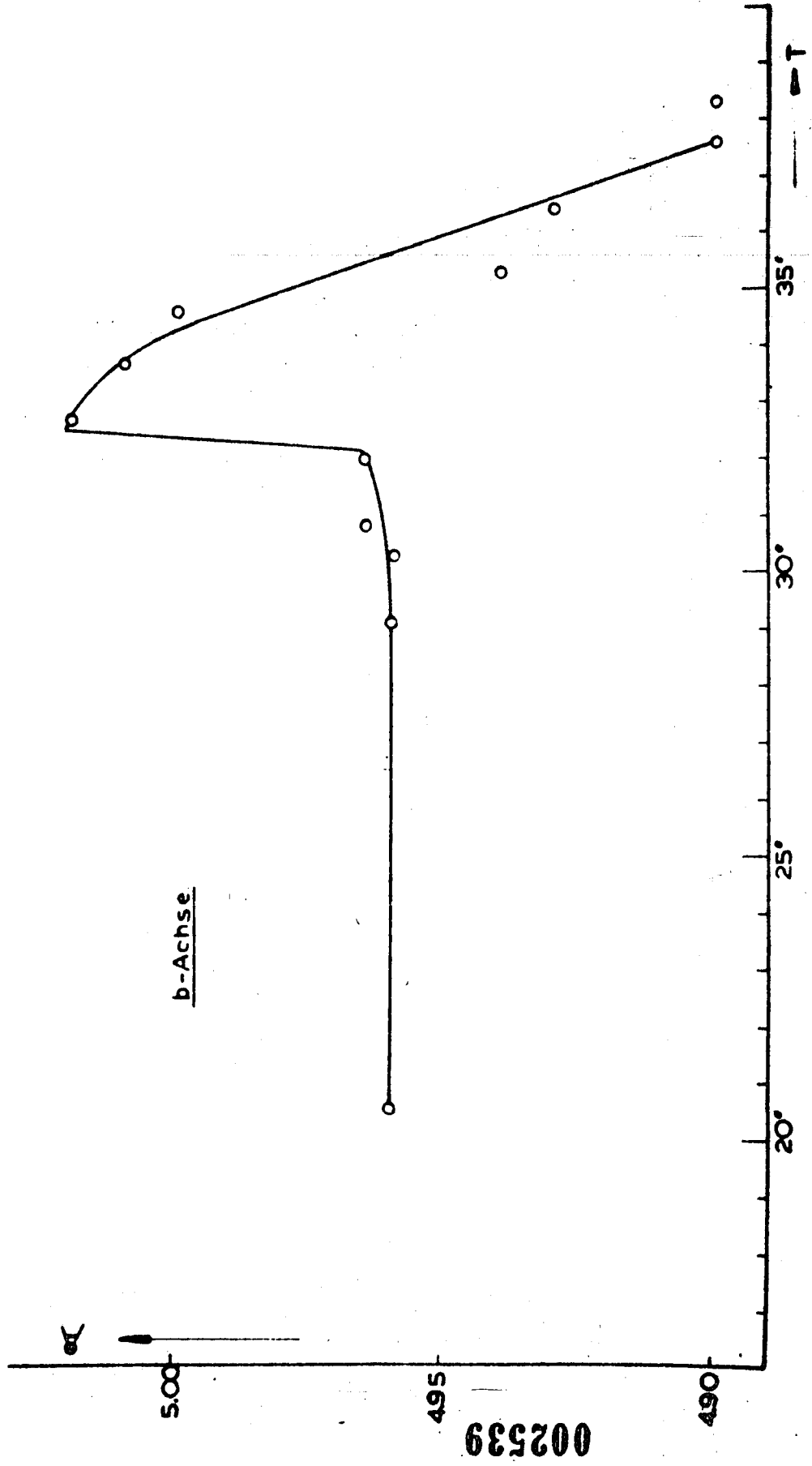


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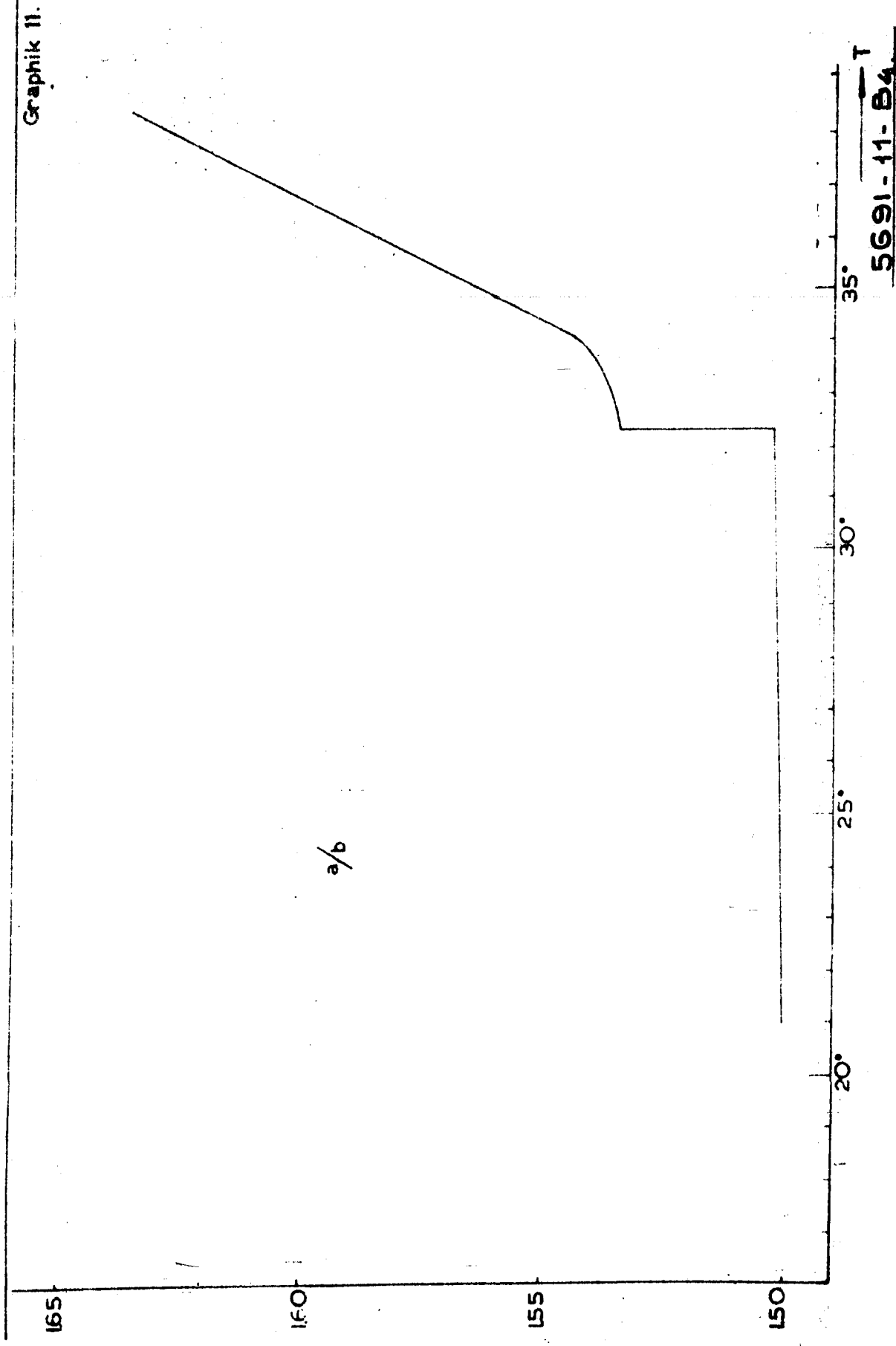
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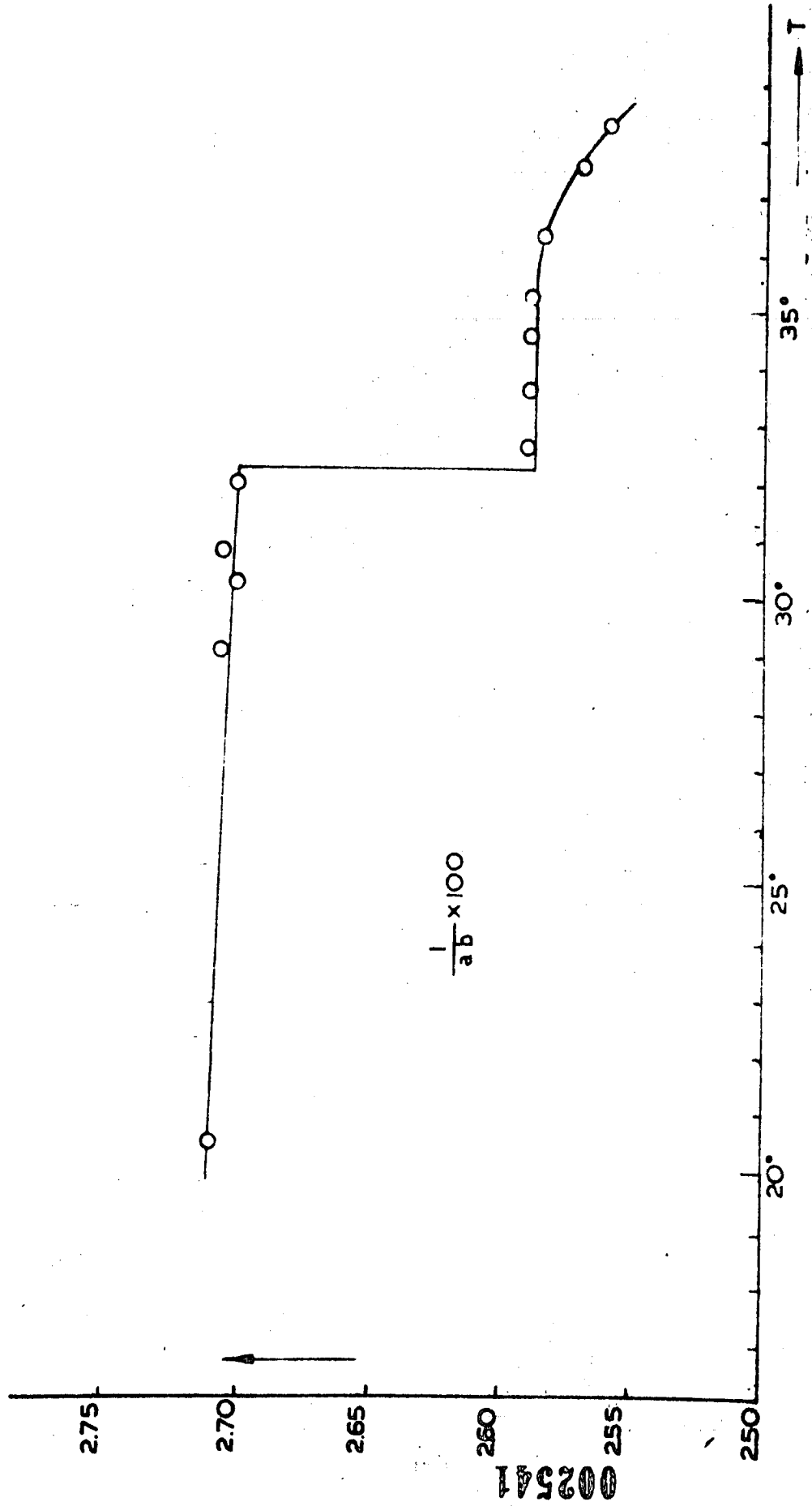
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Graphik 13.



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Table XXVI.

Temp. in C	a in Å	b in Å	100 x 1/ab	a/b
20.5	7.43	4.96	2.71	1.50
29.1	7.45	4.96	2.705	1.50
30.3	7.46	4.96	2.70	1.505
30.8	7.45	4.965	2.705	1.50
32	7.46	4.965	2.70	1.50
32.7	7.71	5.02	2.585	1.53
33.7	7.71	5.01	2.59	1.54
34.6	7.72	5.00	2.59	1.545
35.3	7.81	4.94	2.59	1.58
36.4	7.84	4.93	2.585	1.59
37.6	7.93	4.90	2.57	1.62
38.3	7.97	4.90	2.56	1.63

In Graph IX the length of the a-axis is found, in Graph X the length of the b-axis, in Graph XI the values for a/b, and in Graph XIII the value for 100/ab is set up against the temperature.

The motive for the values found is given to which of the following conclusions?

The length of the a-axis increases suddenly as it reaches the b-axis by a good 32 C; this points to the presence of a transition point. After these transition points, the length of the a-axis increases regularly in contrast to the b-axis which decreases. Correspondingly, one finds a continual increase for the value of a/b above the transition point. (Table XXVI, Graph XI). The significance of this information is designated as follows:

In Figure I there is found a perpendicular cross-section through the packing of the paraffin bonds, the surface which the hydrocarbon covers going in the direction indicated by the diagram.

The preferred direction of the molecules ABCD is one other than that of the molecules E and F. In case the molecular bonds begin to rotate around their longitudinal axis, then a corresponding cross-section, as in Figure 1a, will be given in Figure 1b. The molecular points A, B, E, etc. lie then upon a lattice of three equilateral triangles. From this hexagonal form, the proportion of the a-axis to the b-axis is:  $\sqrt{3}:1=1.73$ .

2543

It is evident from the proportion of the values a/b that, at the transition point which is observed at a good 32 C, no hexagonal form is exhibited; these transition points, therefore, do not depend on the fact that the molecular bonds are recovered in rotation. Above these transition

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FIG. 1<sup>a</sup>

a=7.5

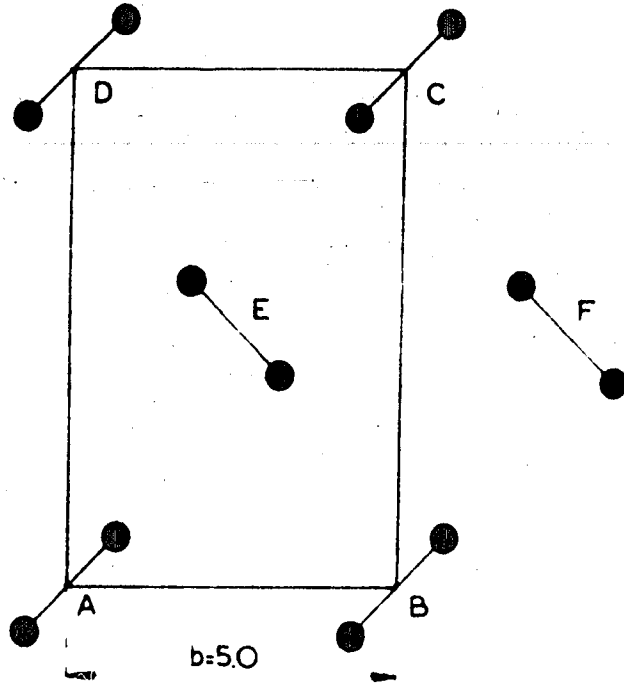
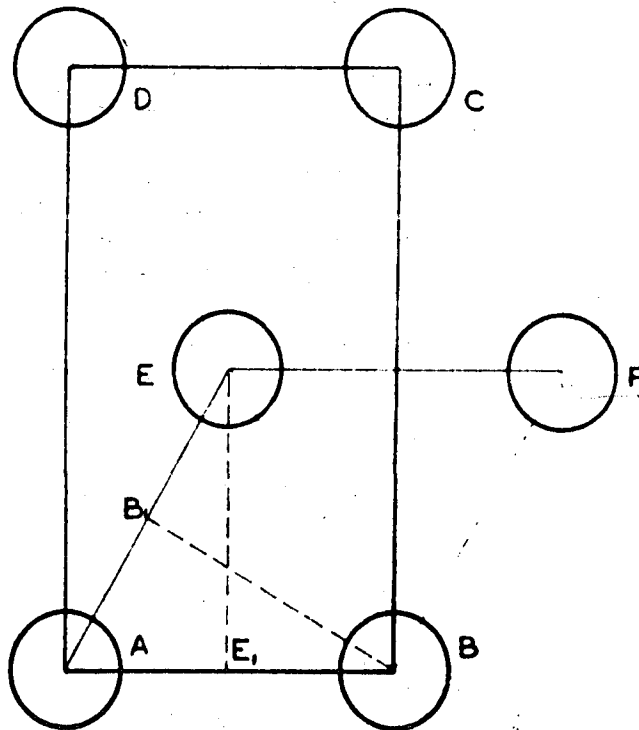
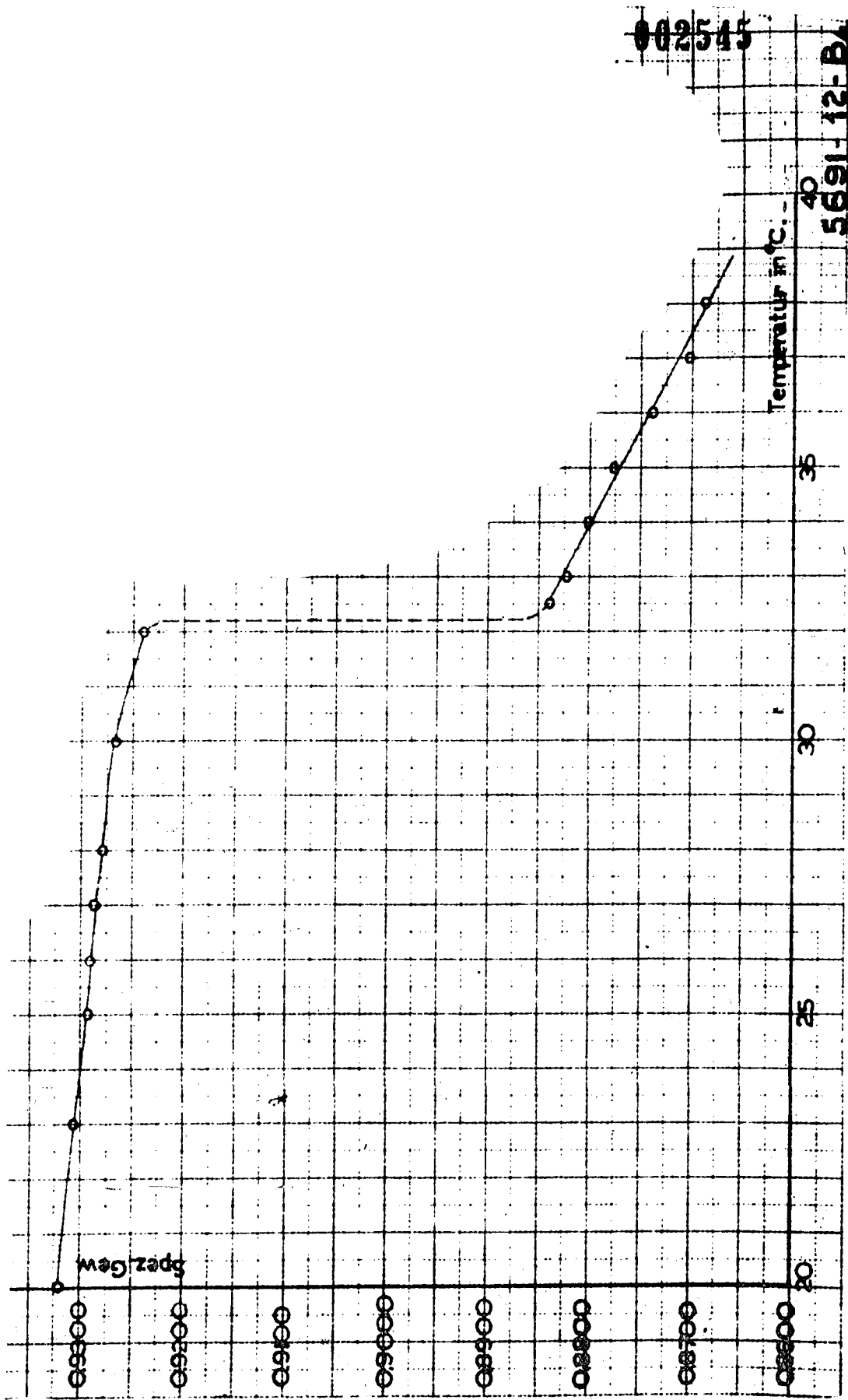


FIG. 1<sup>b</sup>





are points, however, /others that we have already represented as the a- and b-axis in the sense that the proportion a/b always nears the value  $\sqrt{3}:1 = 1.73$ .

Near the melting point the rotation of the molecule in the crystal is therefore incomplete if partial rotation has already occurred. The occurrence of the transition point at 32 C has already yielded the measurement of the specific gravity. In Table XXVII and Graph XII the values of the specific gravity as a function of the temperature are presented. As a check for the specific gravity determined in a pycnometer, the specific gravity was calculated upon a dilatometer panel.

Table XXVII

Temp. in C	$\frac{d}{40}$	
	Pycnometer	Dilatometer
20	0.9518	
23	0.9306	0.9304
25	0.9290	0.9295
26	0.9291	
27	0.9285	
28	0.9279	
30	0.9265	0.9265
32	0.9237	
32.5	0.8858	0.8850
33	0.8821	
34	0.8800	
35	0.8777	
36	0.8758	
37	0.8704	
38	0.8686	

A sudden change in specific gravity occurs between 32 and 32.5; if the value of 0.9237 at 32 C is compared with that of 0.8858 at 32.5 C, a change of 4.3 per cent is evident.

2546

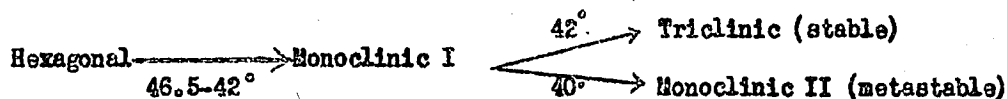
Also the value  $1/ab$ , which is derived from the X-ray photograph, displays a sudden change if it is plotted as a function of the temperature (Graph XIII). The value  $1/ab$  represents an amount for the density of the hydrocarbon. If the change is calculated as  $1/ab$  between a temperature of 32 C and 32.7 C, where these values range from 2.70 up to 2.585, then a break is found of 4.1 per cent. The correspondence of the X-ray photograph method and the pycnometer method for the calculation of the values is satisfactory.

Herewith it is definitely proven that the observation of A. Muller (1) had not been made with a pure product. This observation is, namely: " $C_{21}H_{44}$  behaves in the same way as  $C_{23}H_{48}$ " and, concerning  $C_{25}H_{50}$ : "The transition from the less symmetrical form into the hexagonal close packing is a continuous function of the temperature."

A sharper transition point was found with our product, which did not coincide with the beginning of the rotation of the long molecular bonds. The course of the a/b curves proves that the hexagonal proportion (2): 1 below the approximate melting point, was not attained; the rotation was not complete, therefore, before the melting point was reached.

An analogous X-ray investigation was followed through with the normal hydrocarbon  $C_{24}H_{50}$ . In literature it is given that the modification, monoclinic type II, is stable at room temperature and at 40 C changes over into monoclinic type I; then between 40 and 44 a gradual transition shall occur to the hexagonal form. From this investigation a complicated proportion of the hydrocarbons results. Now the essential point, that has been found by this investigation, will be treated.

The scheme of the different modifications appears as follows:



The temperatures given in these transition schemes relate to the cooling of the hydrocarbons; upon warming, the transition from triclinic to monoclinic occurs first at approximately 45 C. We will return later to this phenomenon. 2547

The following values were established for the cell measurements:

Triclinic Modification at Room Temperature:

$$\begin{array}{ll} a = 7.42 \text{ \AA} & \alpha = -(b, c) = 102^\circ \\ b = 5.35 \text{ \AA} & \beta = -(c, a) = 99.5^\circ \\ c = 32.5 \text{ \AA} & \gamma = -(a, b) = 99^\circ \end{array}$$

Monoclinic II Modification at Room Temperature:

$$\begin{array}{ll} a = 7.50 & \\ b = 4.99 & \beta = 94^\circ \\ c = 32.7 & \end{array}$$

Monoclinic Modification at 42:

$$\begin{array}{ll} a = 7.94 & \\ b = 4.95 & \beta = 94^\circ \\ c = 33.2 & \end{array}$$

Hexagonal Modification at 46.5:

$$\begin{array}{l} a = 4.77 \\ b = 33.3 \end{array}$$

(1) Proc. Roy. Soc. London A 139, 514 (1932).

(2) A. Muller, Proc. Roy. Soc. London A 138, (1932).



In Table XXVIII below, the area of the perpendicular cross-sections of the cells at various temperatures, the length of the c-axis and the volume,  $v$ , calculated thereupon are given. The molecular volume of the substance is thereby calculated by multiplication of the number by the Avogadro number ( $0.603 \times 10^{24}$ ) and dividing by two (the number of molecules per cell).

Table XXVIII

Modification	T in C	Area of the Perpendicular Cross Sect.	c-Axis	V	V in cm <sup>3</sup>
Triclinic	20.0	37.5 $\mu^2$	32.5 $\mu$	1.22 $10^5 \mu^3$	560
	30.5	37.6 "		1.22 "	
	35.7	37.8 "		1.23 "	
	38.5	37.6 "		1.22 "	
	41.0	37.9 "	32.5 $\mu$	1.23 "	571
Monoclinic I	42.0	38.9 "	33.2 $\mu$	1.29 "	589
	44.2	39.6 "		1.32 "	596
Hexagonal Metastable	46.6	39.4 "	33.3 $\mu$	1.31 "	595
Monoclinic II	20.0	36.6 "	32.7 $\mu$	1.20	567

The values determined for the specific gravity by the pycnometer method and those values calculated from them for the molecular volume follow in Table XXIX. These values were determined starting at room temperature and rising to a higher temperature. 2548

Table XXIX

Temp. in C	d t° 4°	Mol. Vol. in cm	Temp. in C	d t° 4°	Mol. Vol. in cm
20	0.9395	530.2	45	0.9280	504.5
25	0.9379	530.8	46	0.9200	507.8
50	0.9351	531.5	46.4	0.9112	512.4
			47	0.8798	-
35	0.9343	532.2	47.2	0.8750	506.7
			38	0.9337	532.4
40	0.9326	532.8		0.8689	-
			47.5	0.8693	509.7
			47.8	0.8677	-
42	0.9322	533.0	48	0.8674	509.1
			48.3	0.8672	-
43.5	0.9319	533.1	48.5	0.8669	509.5
			49.0	0.8661	-
44.5	0.9311	533.4	49.5	0.8656	509.8

In Graph XIV the specific gravity is shown as a function of the temperature; wherefore, one can see that the molecular volume calculated from the pycnometer and the X-ray photographic method correspond.

Since the first named value is obtained upon warming and the second upon cooling of the material, the transition temperatures are not the same. Even the absolute values of the molecular volume obtained by the X-ray photographic method were higher than the others, since these absolute values in favorable conditions can be calculated within 1 per cent. The difference in molecular volume amounts to approximately 6.5 per cent between 41 and 46 by the X-ray method and by the pycnometer method, between 44.5 and 47.5, to about 7 per cent. This conformity is satisfactory.

The specific gravity and the molecular volume, determined by pycnometer and X-ray methods, are set up against the temperature in Graph XIV.

In Graph XV the specific gravity of normal  $C_{24}H_{50}$  is plotted as the function of the temperature, where the measurement is given at increased 2549 as well as decreased temperatures, is shown. It is clearly visible that the transition temperature is not the same upon heating and upon cooling of the material.

At various points on the graph the time is given during which the preparation of the preparation was held at a determined temperature before the gravity determination.

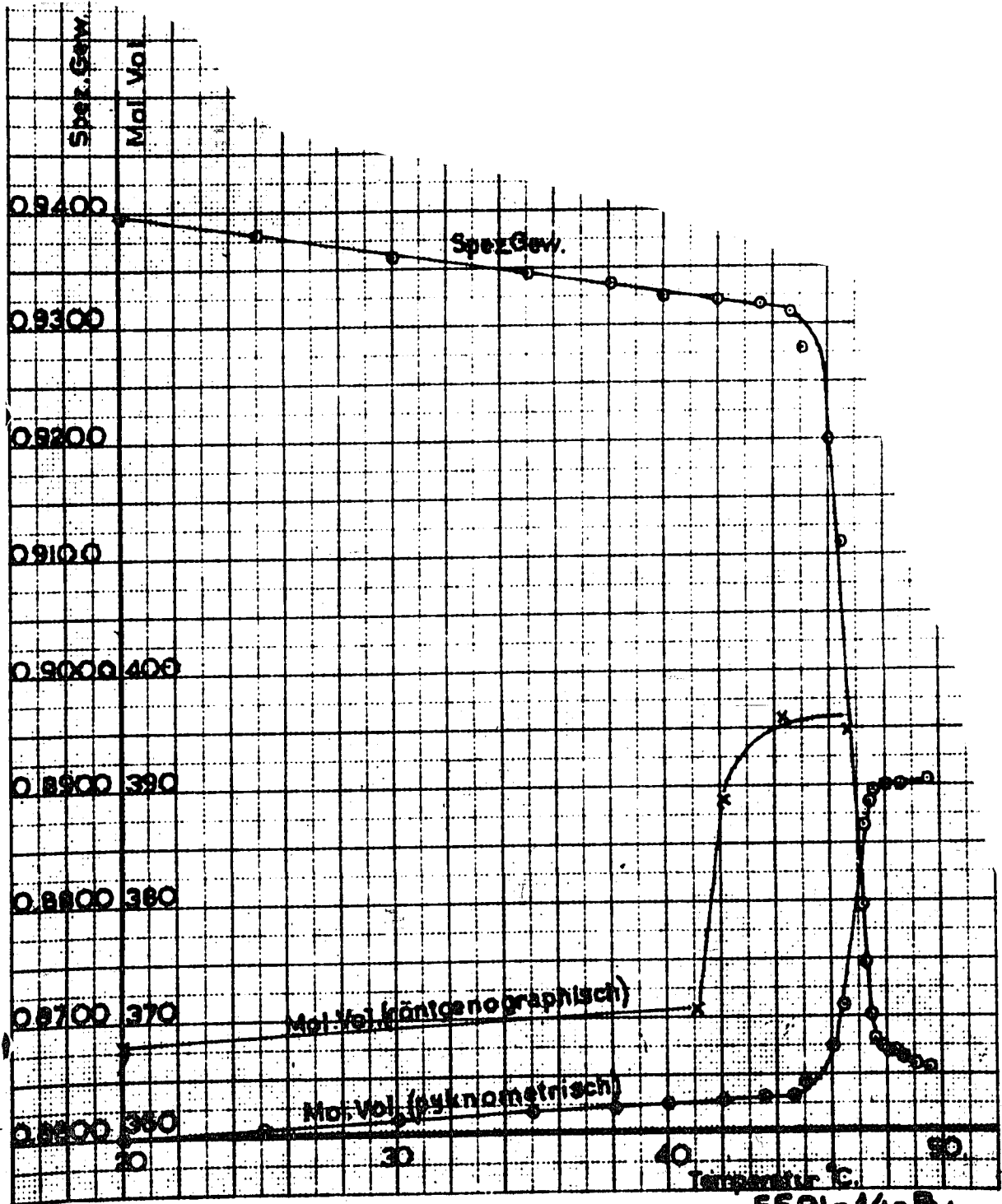
The values are partially given in Table XXX.

Table XXX

Specific gravity of  $C_{24}H_{50}$ , increased to higher temperatures and decreased to lower temperatures.

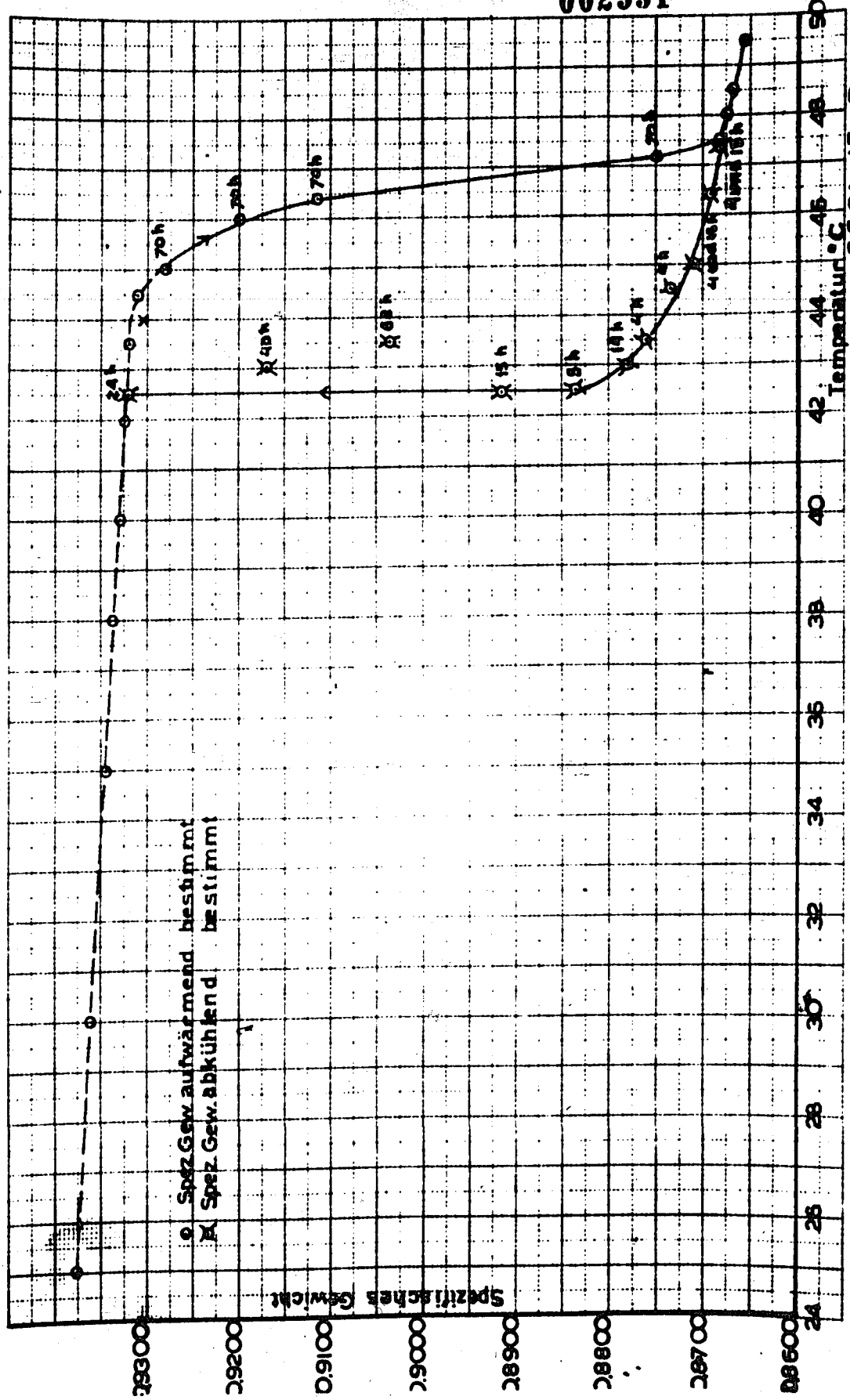
$t$ in C	$d \frac{t}{4}^{\circ}$	Hrs. held at Meas. Temp.	$t$ in C	$d \frac{t}{4}^{\circ}$	Hrs. held at Meas. Temp.
48	0.8674		43.5	0.9037	68
47.4	0.8684		43.0	0.8782	14
46.4	0.8695	4 and 15	43.0	0.9169	40
45.0	0.8712	4 and 15	42.5	0.8837	5
44.5	0.8738	4	42.5	0.8917	15
43.5	0.8766	4	42.5	0.9325	24

From the observation at 43.5 C, at 43.0 C and at 42.5 C it is clearly visible the specific gravity found is dependent upon the time during which the preparation has been held at the measuring temperature. The transformation into the stable modification at lower temperatures occurs very



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Graphik 15.



○ Spez. Gew. aufwärmend bestimmt  
 × Spez. Gew. abkühlend bestimmt

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slowly. The hysteresis rise, which one can obtain, is therefore wholly dependent on the thermal prehistory of the substance.

The specific gravity of various other hydrocarbons in the solid states was determined at other temperatures. No X-ray analysis was made of these paraffins.

The results are summarized in the tables to follow.

Table XXII

Specific Gravity of  $n\text{-C}_{29}\text{H}_{48}$ , Tricosane

2552

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
20	0.9370	-	38	0.9268	0.9272
25	0.9351	-	40	0.8812	0.8807
30	0.9326	0.9327	42.5	0.8728	-
35	0.9295	0.9296	45	0.8647	-

Table XXIII

Specific Gravity of  $n\text{-C}_{28}\text{H}_{58}$ , Octacosane

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
			50	0.9245	0.9265
25	0.9400		52.5	0.9217	
30	0.9370	0.9379	53.5	0.9208	
35	0.9341	0.9352	55	0.8777	
40	0.9317	0.9350	57.5	0.8723	
45	0.9281	0.9301	60	0.8673	0.8684

Table XXIV

Specific Gravity of  $n\text{-C}_{30}\text{H}_{62}$ , Triacontane

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
20	0.9405		47.5	0.9252	
25	0.9385		48.5	0.9245	
30	0.9358	0.9358	50	0.9232	
35	0.9328	0.9328	55	0.9184	

(Continued)

Table XXXIII (Continued)

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
39	0.9514		57.5	0.9151	
40	0.9504	0.9297	59	0.8777	
42.5	0.9289		60	0.8765	0.8752
45	0.9268	0.9278	62.5	0.8708	0.8692
46	0.9268				

Table XXXIV

2553

Specific Gravity of n-C<sub>31</sub>H<sub>64</sub>, Hentriacontane

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
20	0.9434		47.5	0.9292	
25	0.9418		48.5	0.9288	
30	0.9395		50	0.9274	0.9286
35	0.9357		55	0.9233	0.9247
38	0.9348		57.5	0.9206	
40	0.9342		60	0.9154	
42.5	0.9324		61	0.8887	
45	0.9310	0.9317	62.5	0.8786	
48	0.9304		68	0.8707	

Table XXXVSpecific Gravity of n-C<sub>34</sub>H<sub>70</sub>, Tetratriacontane

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
20	0.9488		60	0.9272	0.9268
25	0.9471		62.5	0.9238	
30	0.9455		64.5	0.9200	
35	0.9432		67.5	0.9160	
40	0.9405	0.9399	68.5	0.8926	
45	0.9374	0.9375	69.5	0.8769	0.8763
50	0.9343	0.9345	70	0.8760	
55	0.9312	0.9308	71	0.8743	
57.5	0.9291				

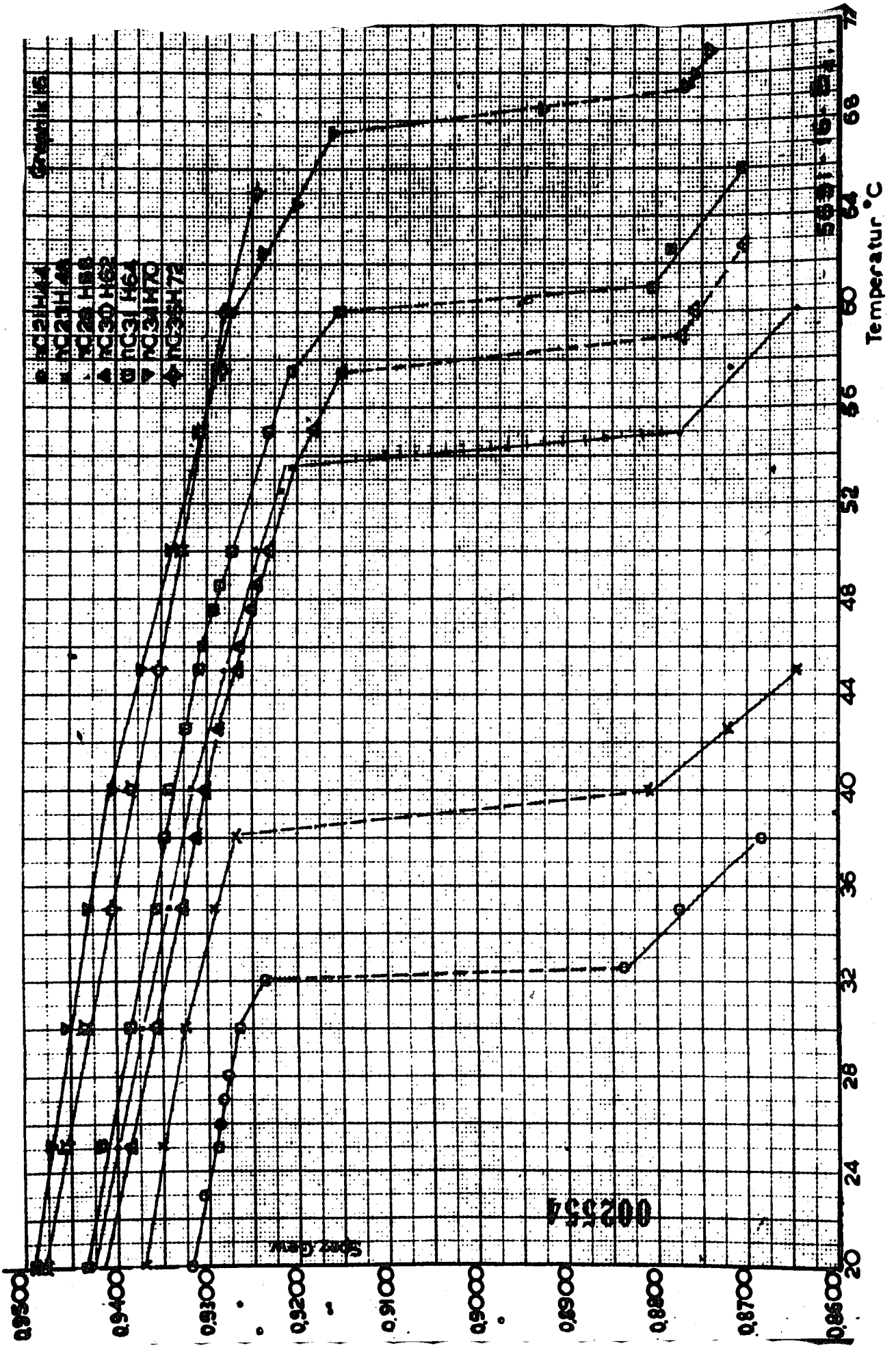


Table XXXVI

Specific Gravity of  $n\text{-C}_{35}\text{H}_{72}$ , Pentatriacontane

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
20	0.9478		50	0.9350	0.9358
25	0.9457		55	0.9307	0.9310
30	0.9436	0.9436	57.5	0.9287	
35	0.9405	0.9413	60	0.9277	0.9277
40	0.9382	0.9389	65	0.9245	
		0.9365			

Table XXXVII

Specific Gravity of  $n\text{-C}_{43}\text{H}_{88}$ , Tritetracontane

2555

Temp. in C	Pycnometer	Dilatometer	Temp. in C	Pycnometer	Dilatometer
20	0.9589		55	0.9418	0.9422
25	0.9570		57.5	0.9395	
30	0.9552	0.9548	60	0.9381	0.9381
35	0.9530	0.9525	62.5	0.9361	
40	0.9507	0.9500	64.5	0.9350	
45	0.9480	0.9479	67.5	0.9323	
50	0.9451	0.9452	70	0.9296	0.9295
55	0.9418	0.9422	75	0.9227	0.9228

In Graph XVI the specific gravities are represented as a function of the temperature. The gradual change in specific gravity at a determined temperature, in all cases, is very clear. The existence of a sharp transition point will, therefore, be proved in other ways. It is noticeable that, if one compares the specific gravities of the solid materials at, for example, 30 C,  $n\text{-C}_{50}\text{H}_{102}$  has a lower specific gravity than  $n\text{-C}_{23}\text{H}_{48}$  and  $n\text{-C}_{35}\text{H}_{72}$  a lower specific gravity than  $n\text{-C}_{32}\text{H}_{70}$ .

If it is certain that the occurrence is real, then a more thorough investigation is necessary.

A difficulty encountered in the specific gravity determination of all hydrocarbons with a transition point is the following: in order that the hydrocarbon be completely free of air in the pycnometer, it is necessary to deaerate the melted substance in the pycnometer. If this is followed, then



de-aerated water is let into the vacuum. The melted material will become solid on cooling and transpose after a time into the modification that is stable at lower temperatures, which brings with it a considerable change in volume. It is easily conceivable that cavities exist in the paraffin, which are not attainable for water, so an incorrect measurement of the specific gravity has to follow.

VII. Determination of the Solubility of Hydrocarbons  
I. The Solubility of n-Heneicosane in  
2,2,4-Trimethylpentane (Iso-octane)

Various amounts of n-C<sub>21</sub>H<sub>44</sub> were introduced into a glass tube in which pure 2,2,4-trimethylpentane was found. This tube was sealed and warmed in water under continuous agitation. The heating took place very slowly. The moment was observed in which the last bit of hydrocarbon dissolved. The results of this experiment are summarized in Table XXXVIII.

Table XXXVIII

Solubility of n-C<sub>21</sub>H<sub>44</sub> in 2,2,4-Trimethylpentane

Amt. C <sub>21</sub> H <sub>44</sub> in Mol. %	Temp. in C	log X	1/T <sub>s</sub> - 1/T
6.88	10.2	0.8375	-3393 x 10 <sup>-7</sup>
11.62	15.0	1.0652	-2809 x 10 <sup>-7</sup>
20.75	20.7	1.5170	-2133 x 10 <sup>-7</sup>
40.61	27.7	1.6086	-1339 x 10 <sup>-7</sup>
64.07	33.0	1.8067	- 762 x 10 <sup>-7</sup>

The relation between temperature and solubility in an ideal situation (when the heat of mixing and the change in volume are zero) is represented by the equation:

$$\ln x = Q/R (1/T_s - 1/T)$$

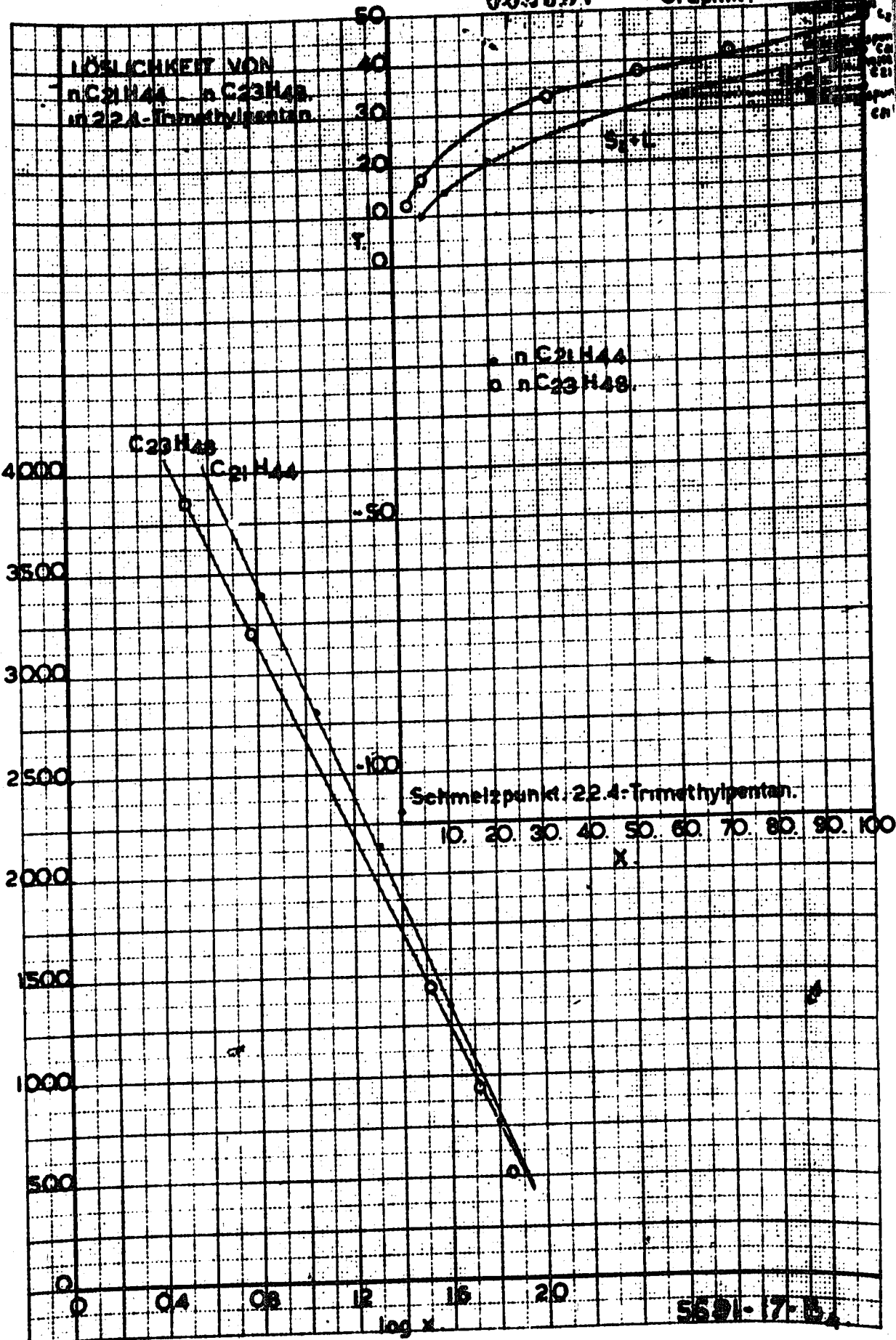
In this case x is the concentration in mol. per cent of the hydrocarbon, T<sub>s</sub> the melting temperature in absolute degrees and T the temperature at which the material dissolves.

If ln x is set up graphically against 1/T<sub>s</sub> - 1/T, then a straight line is obtained. From Graph XVII it is clear that it is possible to draw a straight line through a great part of the investigated region. The likeness, according to Clapyron, is thus practicable above a greater concentration area. Also in Graph XVII is designated the T-x figure of

002557

Graphik. 17.

LÖSLICHKEIT VON  
nC<sub>21</sub>H<sub>44</sub> - nC<sub>23</sub>H<sub>48</sub>  
in 2,2,4-Trimethylpentan



$$-\left(\frac{1}{T_s} - \frac{1}{T}\right) \times 10^7$$

$\log x$

5591-17-13

normal heneicosane with 2,2,4-trimethylpentane. As it can be seen, the point determined at the highest concentration shall lie directly upon the fusion curve which reaches stable modification at higher temperature.

## II. The Solubility of n-Tricosane in 2,2,4-Trimethylpentane

2558

The values for the solubility of normal tricosane can be found in Table XXXIX.

Table XXXIX

Solubility of n-Tricosane in 2,2,4-Trimethylpentane

Amt. n-C <sub>23</sub> H <sub>48</sub> in Sol. %	Temp. in C	log X	1/T <sub>0</sub> - 1/T
3.26	12.2	0.5130	-3849 x 10 <sup>-7</sup>
6.10	17.5	0.7855	-3201 x 10 <sup>-7</sup>
52.99	33.3	1.5182	-1435 x 10 <sup>-7</sup>
52.38	38.0	1.7192	- 954 x 10 <sup>-7</sup>
71.77	42.1	1.8560	- 523 x 10 <sup>-7</sup>

Also, at these conditions, from Graph XVII it results that the equation of Clapyron corresponds to a greater concentration area. The point determined at the highest concentration lies upon fusion line of the modification stabilized under the melting point, as is seen from the T-x figure in Graph XVII.

## III. The Solubility in Acetone

Pure acetone was heated for an hour with ignited calcium carbonate. Following this, the acetone was distilled and collected in a stock bottle, free from moistened air.

The values found for the solubility are found in Table XL. It turns out that at a concentration of 4.60 mol per cent n-tetracosane and a temperature of 44.7 C two liquid phases occur. Between 44.7 and 54.3 C an equilibrium prevails between these two liquid phases, above 54.3 these two phases are again identical. Other points in the disintegration area were not investigated. It can be concluded from Graph XVIII that the equation of Clapyron applies above a very small concentration area. Consequently there is, as a result, a deviation of the approximation of the disintegration area.

Table XI.

## Solubility of n-Tetracosane in Acetone

Amt. n-C <sub>24</sub> H <sub>50</sub> in Mol %	Temp. in C	log x	1/T <sub>g</sub> - 1/T	Amt. n-C <sub>24</sub> H <sub>50</sub> in Mol %	Temp. in C	log x	1/T <sub>g</sub> - 1/T
0.00145	4.4	-2.8373	-5152 x 10 <sup>-7</sup>	0.0552	26.1	-1.2581	-2535 x 10 <sup>-7</sup>
0.00183	5.7	-2.7367	-4984 x 10 <sup>-7</sup>	0.114	30.5	-0.9457	-2051 x 10 <sup>-7</sup>
0.00287	9.4	-2.5415	-4511 x 10 <sup>-7</sup>	0.223	34.4	-0.6522	-1634 x 10 <sup>-7</sup>
0.00602	13.7	-2.2205	-3988 x 10 <sup>-7</sup>	0.420	37.0	-0.5771	-1361 x 10 <sup>-7</sup>
0.0147	19.7	-1.8321	-3273 x 10 <sup>-7</sup>	0.910	41.9	-0.0409	- 864 x 10 <sup>-7</sup>
0.0166	20.5	-1.7797	-3193 x 10 <sup>-7</sup>	1.84	44.4	-0.2655	- 612 x 10 <sup>-7</sup>
0.0307	23.1	-1.5128	-2876 x 10 <sup>-7</sup>	4.61	54.3(1)	-0.6635	- 343 x 10 <sup>-7</sup>
0.0508	23.2	-1.5116	-2869 x 10 <sup>-7</sup>				

(1) Temperature at the exact disappearance of the disintegration.

Again in Graph XVIII a T-x figure is given with the possible location of the beginning of disintegration. Since only one point was determined, the location cannot be established with surety.

## b. Solubility in Ethanol

Absolute ethanol was heated for an hour with calcium flakes; then the alcohol was distilled off. The distilled alcohol was treated with dry tartaric acid in order to combine eventually with ammonia present (from calcium nitrite and water). The alcohol is redistilled. The results of the solubility determinations are given in Table XII.

Table XII

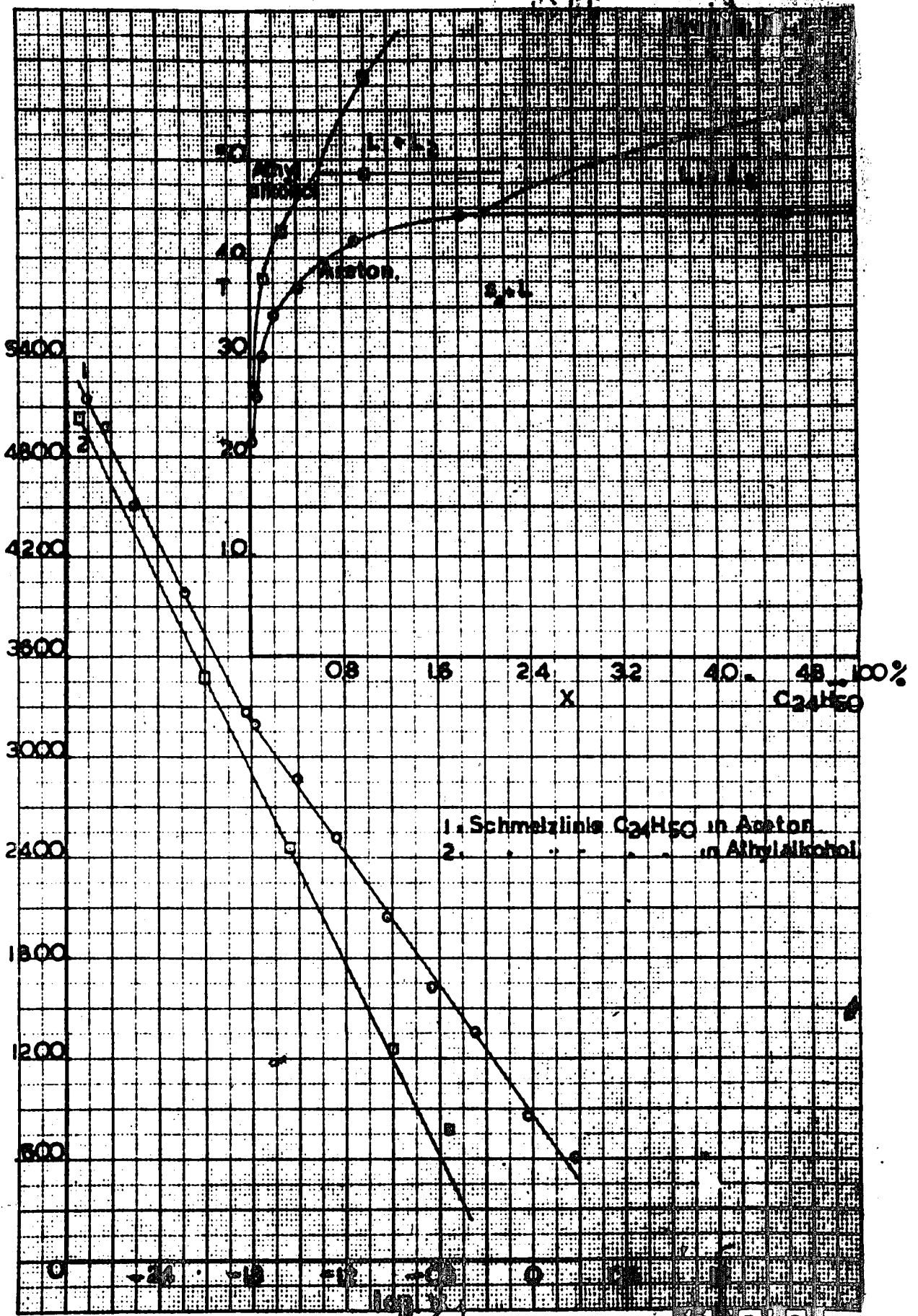
## Solubility of n-Tetracosane in Ethanol

Amt. n-C <sub>24</sub> H <sub>50</sub> in Mol %	Temp. in C	log x	1/T <sub>g</sub> - 1/T
0.00128	5.2	-2.8953	-5043 x 10 <sup>-7</sup>
0.00795	17.9	-2.1022	-3485 x 10 <sup>-7</sup>
0.0200	26.8	-1.5523	-2462 x 10 <sup>-7</sup>
0.125	38.0	-0.9045	-1265 x 10 <sup>-7</sup>
0.293	42.7	-0.5331	- 779 x 10 <sup>-7</sup>
1.042 (1)	53.5	0.0178	- 729 x 10 <sup>-7</sup>

(1) At these temperatures the two coexisting liquid phases become identical.

002560

$$-\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \times 10^7$$



1931-10-14

It is to be noticed that at a concentration of 1.04 mol per cent of hydrocarbon and a temperature of 48.9 C two liquid phases occur, which become identical at 53.5 C. From Graph XVIII it can easily be seen that the equation of Clapyron is only applicable over a small area. The disintegration disturbs the course of the fusion curve. In the T-x figure the probable course of the beginning of the disintegration is shown.

#### c. Solubility in Chloroform

Chemically pure chloroform was distilled shortly before the solubility determinations. The results of the determinations are set forth in Table XLII.

Table XLII

Solubility of n-Tetracosane in Chloroform

Amt. n-C <sub>24</sub> H <sub>50</sub> in Sol	Temp. in C	log x	1/T <sub>2</sub> - 1/T <sub>1</sub>
0.0295	-11.1	-1.5293	-7275 x 10 <sup>-7</sup>
0.174	- 0.5	-0.7605	-5772 x 10 <sup>-7</sup>
0.940	10.7	-0.0238	-4343 x 10 <sup>-7</sup>
1.73	14.7	0.2373	-3854 x 10 <sup>-7</sup>
3.69	20.9	0.5871	-3223 x 10 <sup>-7</sup>
14.13	30.1	1.1505	-2095 x 10 <sup>-7</sup>
36.52	39.1	1.5625	-1143 x 10 <sup>-7</sup>

In Graph XIX one sees that the equation of Clapyron is valid over a large concentration area. The T-x figure is also plotted in Graph XIX; in the area of higher concentrations, no points are ascertained; so it is declared that the probable course of the figure is plotted.

#### d. Solubility in 2,2,4-Trimethylpentane

Pure 2,2,4-trimethylpentane was distilled under reduced pressure for these determinations. The results of the solubility determinations are summarized in Table XLIII.

Table XLIII

2562

Amt. n-C <sub>24</sub> H <sub>50</sub> in Mol %	Temp. in C	log x	1/T <sub>g</sub> - 1/T	Amt. n-C <sub>24</sub> H <sub>50</sub> in Mol %	Temp. in C	log x	1/T <sub>g</sub> - 1/T
0.0815	-9.6	-1.0886	-7060 x 10 <sup>-7</sup>	26.88	36.2	1.4262	-1450 x 10 <sup>-7</sup>
0.405	2.0	-0.3928	-5480 x 10 <sup>-7</sup>	38.55	39.9	1.5860	-1069 x 10 <sup>-7</sup>
1.360	11.1	0.1856	-4303 x 10 <sup>-7</sup>	52.13	43.0	1.7171	-754 x 10 <sup>-7</sup>
3.352	18.1	0.5227	-3454 x 10 <sup>-7</sup>	67.06	45.6	1.8264	-494 x 10 <sup>-7</sup>
9.535	26.9	0.9792	-2453 x 10 <sup>-7</sup>	91.85	49.2	1.9631	-142 x 10 <sup>-7</sup>
19.44	35.3	1.2886	-1757 x 10 <sup>-7</sup>				

It appears, from Graph XI, that log x set up against 1/T<sub>g</sub> - 1/T over a large range of concentration can be represented by a straight line, thus proving that the equation of Clapyron is applicable over a large concentration area. The T-x figure displays the normal course of the fusion curve.

#### e. Solubility in Toluene

Pure toluene was subjected to distillation under reduced pressure; then the material was used for the solubility determinations. The results of these determinations are assembled in Table XLIV.

Table XLIV

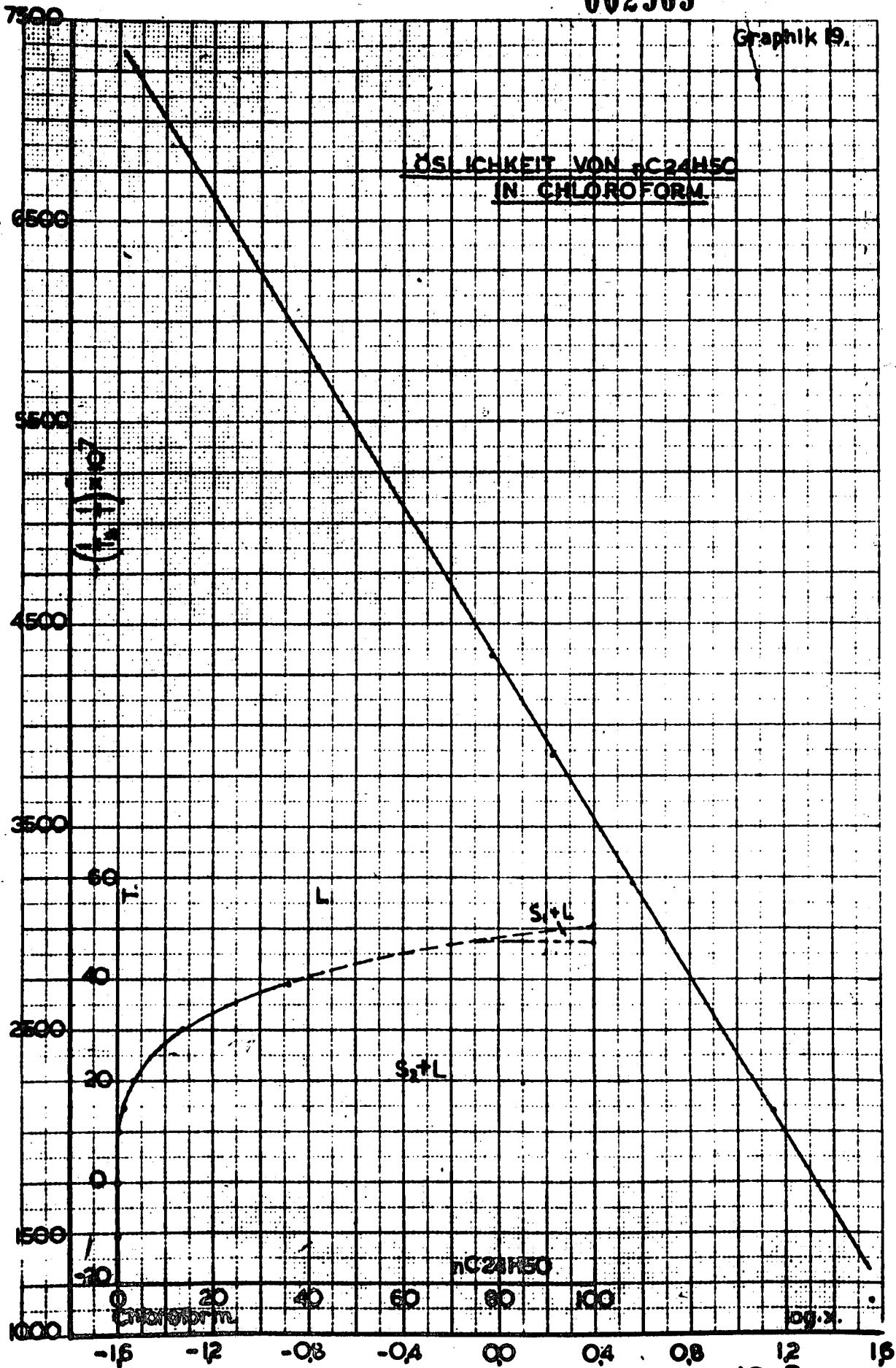
#### Solubility of n-Tetracosane in Toluene

Amt. n-C <sub>24</sub> H <sub>50</sub> in Mol %	Temp. in C	log x	1/T <sub>g</sub> - 1/T
0.103	-5.5	-0.9885	-6493 x 10 <sup>-7</sup>
0.409	3.4	-0.3885	-5280 x 10 <sup>-7</sup>
1.196	10.8	0.0777	-4340 x 10 <sup>-7</sup>
3.944	19.3	0.5960	-3510 x 10 <sup>-7</sup>
13.11	28.8	1.1175	-2238 x 10 <sup>-7</sup>
22.43	33.8	1.3508	-1697 x 10 <sup>-7</sup>
39.75	39.7	1.5993	-1074 x 10 <sup>-7</sup>
86.1	48.3	1.9349	- 233 x 10 <sup>-7</sup>

From Graph XXI it is evident that the equation of Clapyron may be applied to a seemingly large range of concentration, namely, between 0.1 and 13 mol per cent of hydrocarbon. Also, a straight line may be drawn through the points, which comprise the concentration range from 13 up to 86 mol.

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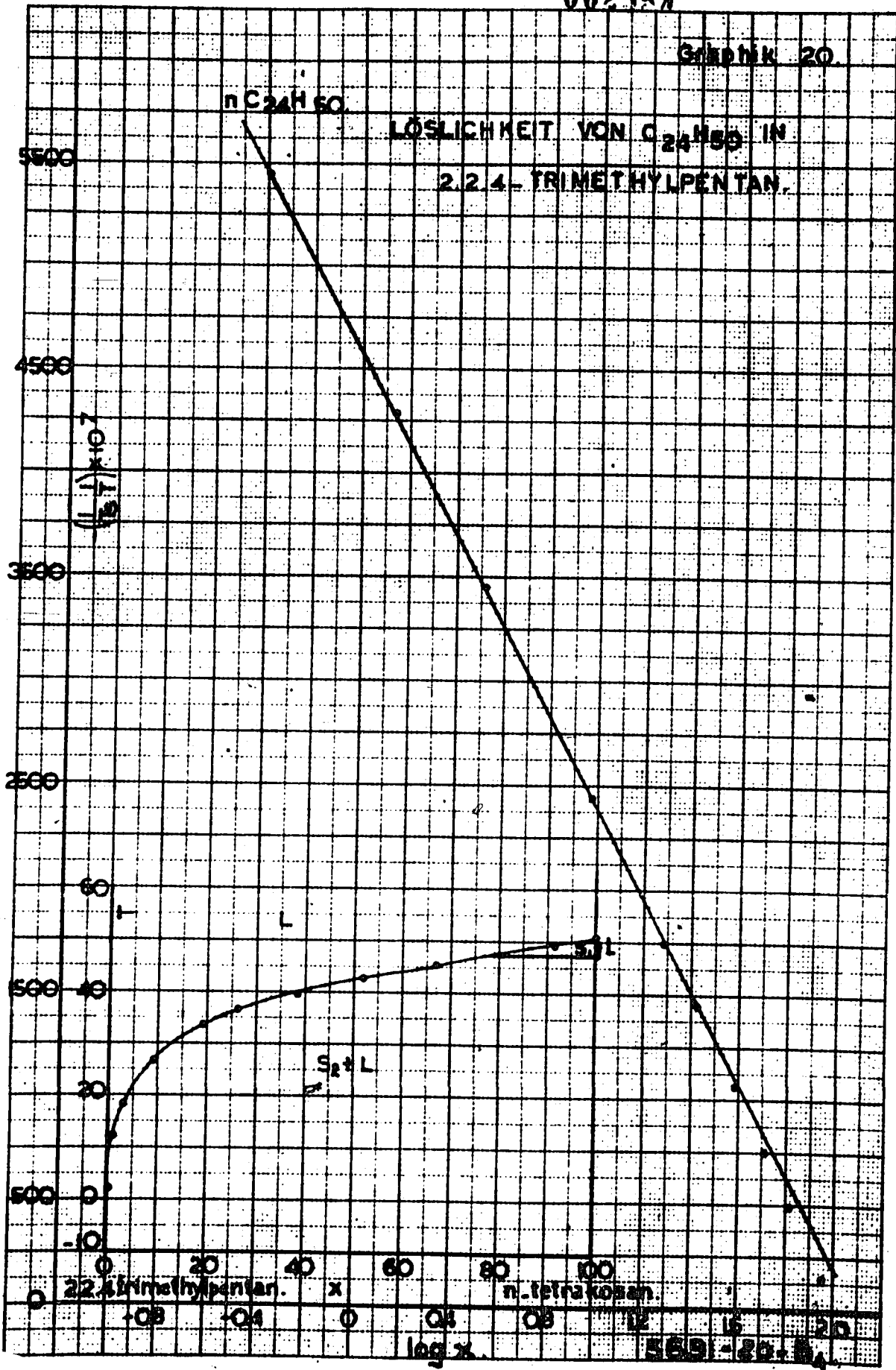
Graphik 19.

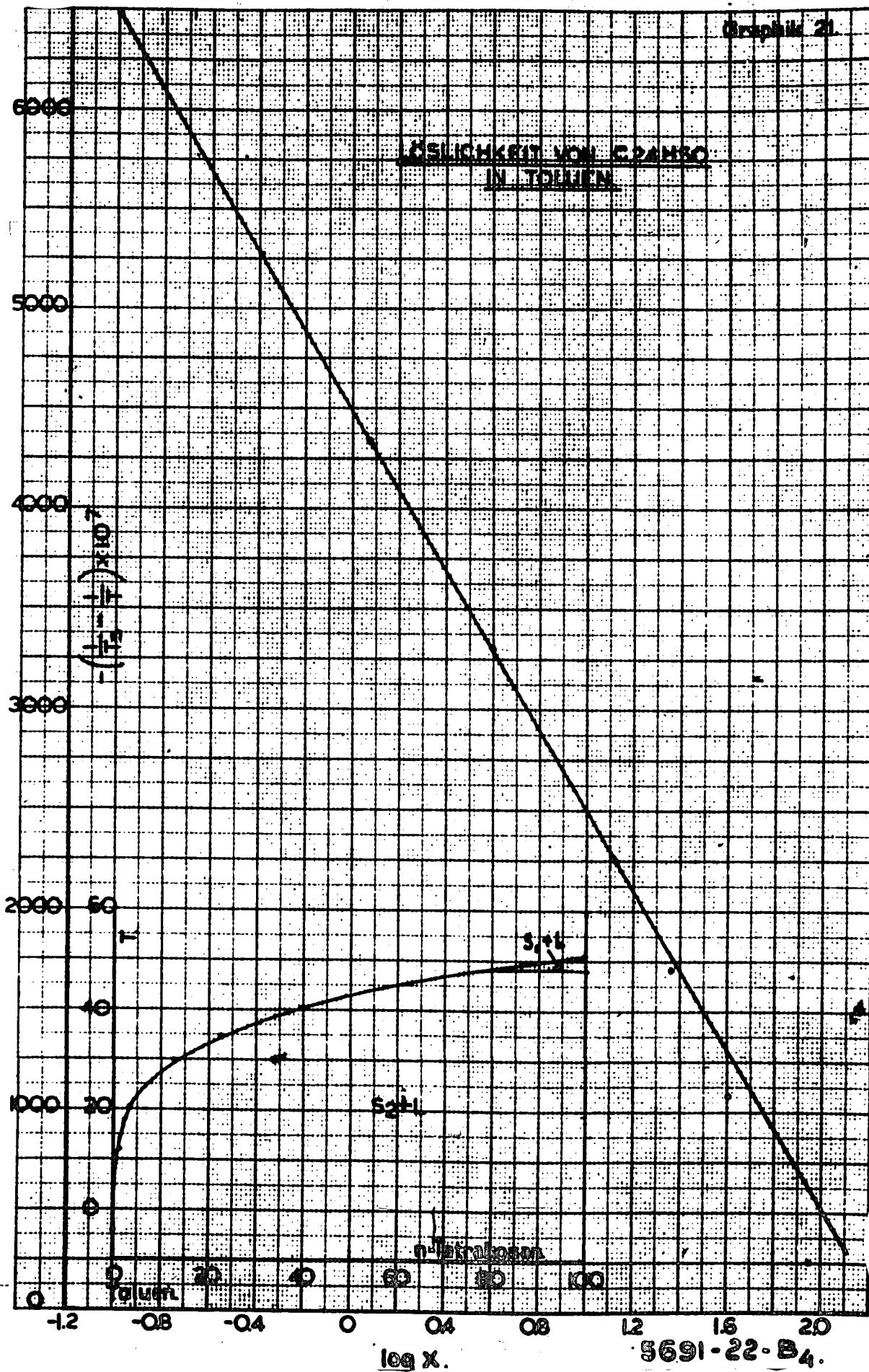




00258A

Graphik 20.





Here again the equation proved correct for a determined area. 2566  
However, it did not apply over the entire concentration range.

The values for the solubility of n-hentriacontane in 2,2,4-trimethylpentane are given in Table XLV.

Table XLV

Solubility of n-C<sub>31</sub>H<sub>64</sub> in 2,2,4-Trimethylpentane

Amt. n-C <sub>31</sub> H <sub>64</sub> in Mol %	Temp. in C	log $\pi$	1/T <sub>s</sub> - 1/T
4.32	39.3	0.6356	-2631 x 10 <sup>-7</sup>
8.17	44.1	0.9123	-2147 x 10 <sup>-7</sup>
14.72	48.4	1.1680	-1725 x 10 <sup>-7</sup>
32.17	54.4	1.5066	-1156 x 10 <sup>-7</sup>
54.31	59.7	1.7349	- 670 x 10 <sup>-7</sup>

The log  $\pi$  is set forth against 1/T<sub>s</sub> - 1/T in Graph XIII. The equation of Clapyron proves correct for the concentration range from 4.3 to 32 mol per cent. The T-x figures exhibit the normal picture of a fusion curve. Here, as in former cases, the range of the higher concentrations of the hydrocarbons was not investigated.

The eutetic lies very one-sided for all investigated hydrocarbons in the solvents 2,2,4-trimethylpentane, chloroform, toluene, acetone and ethanol. The solubility of the solid hydrocarbons in the corresponding solvents becomes slightly extreme at the eutetical temperature.

### THIRD CHAPTER

#### Mixtures of Hydrocarbons

Mixtures of the various hydrocarbons were prepared in order that an insight might be gained into the possibilities presented therefrom.

##### A. Determination of the Viscosities of Mixtures of Hydrocarbons

2567

A mixture of 50 mol per cent n-heneicosane and 50 mol per cent tricosane was prepared and the viscosity measured at 70, 80 and 90 C. In Table XLVI the values found are given together with those of the viscosities of the pure components so that a comparison may be made.

Graphik 22

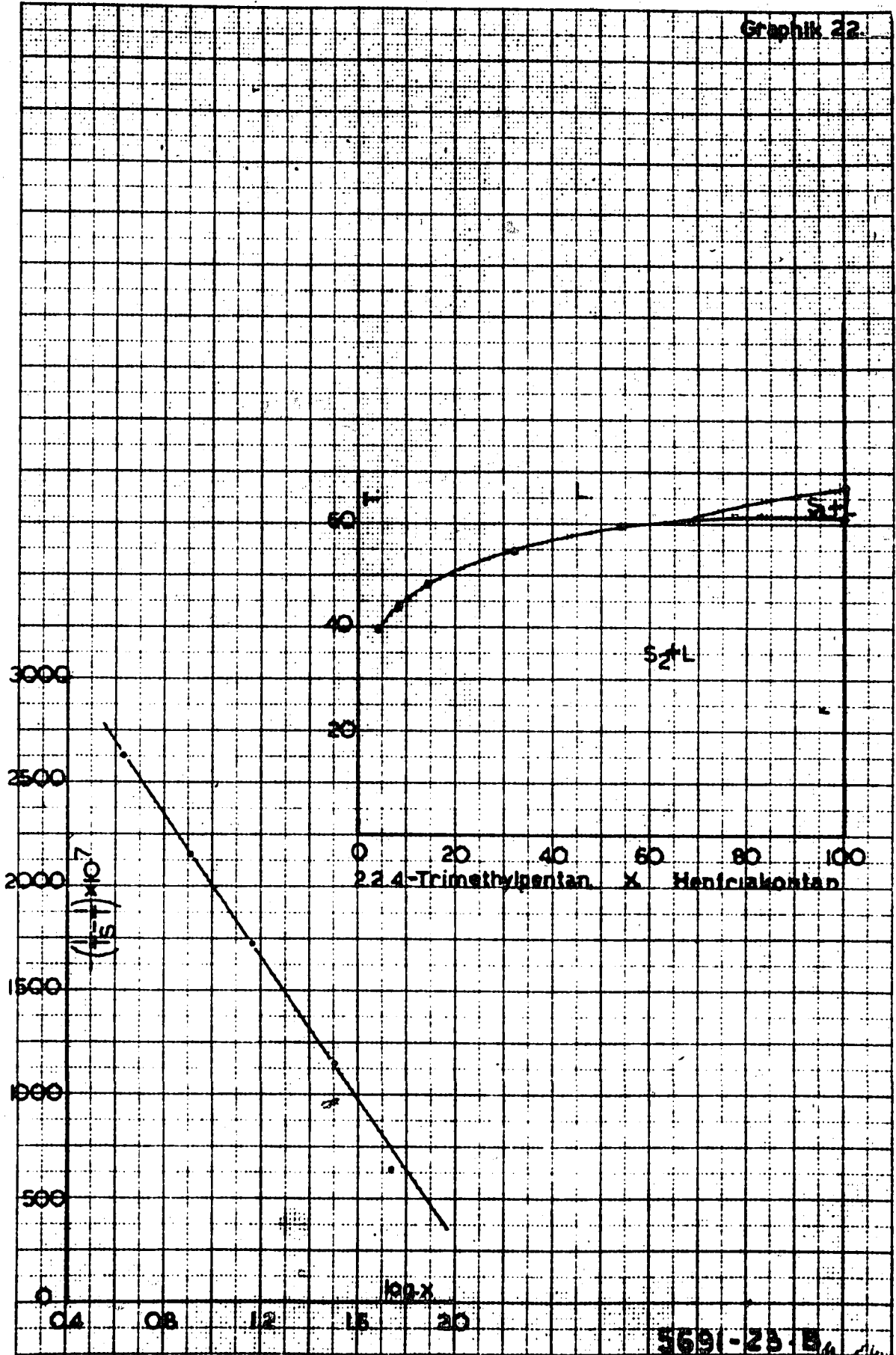


Table XLVI

Temp. in C	Viscosity in Poise n-C <sub>21</sub> H <sub>44</sub>	Viscosity in Poise n-C <sub>25</sub> H <sub>48</sub>	Viscosity Mixture in Poise of 50 Mol % C <sub>21</sub> H <sub>44</sub> and 50 Mol % C <sub>25</sub> H <sub>48</sub>	Viscosity in Poise Acc. to log Equation	Viscosity in Poise Acc. to Fluidity Equation
70	0.0252	0.0312	0.0281	0.0282	0.0280
80	0.0212	0.0261	0.0235	0.0237	0.0236
90	0.0181	0.0220	0.0201	0.0200	0.0199

The values of the viscosities of the mixtures in the next to the last column were calculated according to the logarithmic equation of Arrhenius, which is as follows:

$$\log \eta = V_1 \log \eta_1 + V_2 \log \eta_2$$

in which  $V_1$  and  $V_2$  represent the volume of the components in per cent. The fluidity equation, from which the values in the last column are determined, is thus:

$$1/\eta = V_1/\eta_1 + V_2/\eta_2$$

In the case above, the deviation between the viscosities observed and those calculated from both equations is slight, the largest deviation amounting to 1 per cent.

## 2. Mixtures of n-Henicosane and n-Hentriacontane

Three mixtures were prepared, one with a composition of 25 mol per cent of C<sub>21</sub>H<sub>44</sub> and 75 mol per cent of C<sub>31</sub>H<sub>64</sub>, one with a composition of 50 mol per cent C<sub>21</sub>H<sub>44</sub> and 50 mol per cent C<sub>31</sub>H<sub>64</sub>, and one with a composition of 75 mol per cent C<sub>21</sub>H<sub>44</sub> and 25 mol per cent C<sub>31</sub>H<sub>64</sub>. The values of the measured and calculated viscosities are presented in Table XLVII.

Table XLVII

2569

Temp. in C	Viscosity in Poise n-C <sub>21</sub> H <sub>44</sub>	Viscosity in Poise n-C <sub>31</sub> H <sub>64</sub>	Viscosity of Mixture 25 Mol % n-C <sub>21</sub> H <sub>44</sub> and 75 Mol % n-C <sub>31</sub> H <sub>64</sub>	Viscosity in Poise Acc. to log Equation	Viscosity in Poise Acc. to Fluidity Equation
70	0.0252	0.0660	0.0540	0.0549	0.0503
80	0.0212	0.0535	0.0440	0.0447	0.0415
90	0.0181	0.0437	0.0365	0.0370	0.0345

(Continued)

Table XLVII (Continued)

Temp. in C	Viscosity in Poise n-C <sub>21</sub> H <sub>44</sub>	Viscosity in Poise n-C <sub>31</sub> H <sub>64</sub>	Viscosity of Mixture 50 Mol % n-C <sub>21</sub> H <sub>44</sub> and 50 Mol % n-C <sub>31</sub> H <sub>64</sub>	Viscosity in Poise Acc. to log Equation	Viscosity in Poise Acc. to Fluidity Equation
70	0.0252	0.0660	0.0439	0.0445	0.0397
80	0.0212	0.0535	0.0361	0.0363	0.0331
90	0.0181	0.0437	0.0304	0.0306	0.0278

Temp. in C	Viscosity in Poise n-C <sub>21</sub> H <sub>44</sub>	Viscosity in Poise n-C <sub>31</sub> H <sub>64</sub>	Viscosity of Mixture 75 Mol % n-C <sub>21</sub> H <sub>44</sub> and 25 Mol % n-C <sub>31</sub> H <sub>64</sub>	Viscosity in Poise Acc. to log Equation	Viscosity in Poise Acc. to Fluidity Equation
70	0.0252	0.0660	0.0340	0.0344	0.0315
80	0.0212	0.0535	0.0283	0.0288	0.0265
90	0.0181	0.0437	0.0239	0.0242	0.0224

From the table it appears that the value calculated for the viscosity of the mixture by the logarithmic equation is always too high, the deviation being proportionally slight and always remaining under 2 per cent. The fluidity equation gives a considerably lower value for the calculated viscosity of the mixture.

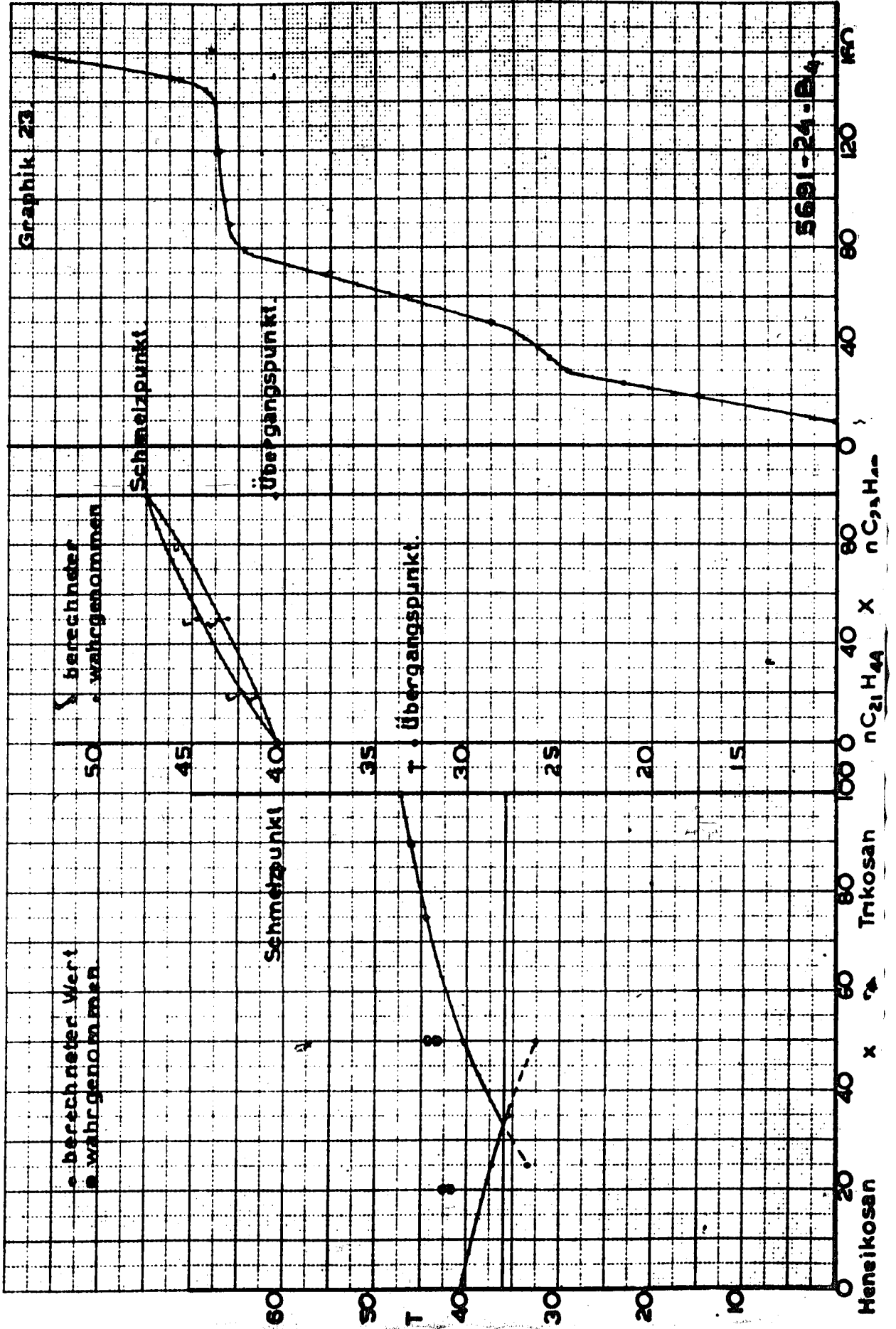
A mixture of 50 mol per cent n-tetracosane and 50 mol per cent 18-methylpentacosane was prepared and the viscosity measured. The values found and those calculated are set up in Table XLVIII.

Table XLVIII

Temp. in C	Viscosity in Poise n-C <sub>24</sub> H <sub>50</sub>	Viscosity in Poise Branched C <sub>26</sub> H <sub>54</sub>	Viscosity of Mixture 50 Mol % n-C <sub>24</sub> H <sub>50</sub> and 50 Mol % br-C <sub>26</sub> H <sub>54</sub>	Viscosity in Poise Acc. to log Equation	Viscosity in Poise Acc. to Fluidity Equation
80	0.0238	0.0324	0.0306	0.0306	0.0306
90	0.0243	0.0271	0.0257	0.0257	0.0256

It can be seen that the calculated value of the viscosity of mixtures both according to the logarithmic and the fluidity equations deviates very little from the actual value. The greatest deviation is approximately 0.4 per cent. 2570

The number of measurements of the viscosities of mixtures has been



too small to justify a general conclusion; in the cases investigated the logarithmic equation seems to be better than the fluidity equation, even when the components of the mixture show a seemingly powerful separate molecular weight.

### B. The Behavior of Several Binary Systems

The fusion curves for these systems were calculated for the ideal situation (that is, that no heat of mixing and no change in volume occurred) from Clapyron's equation. The temperature was calculated at which the solid substance began to crystallize out. The values are given below.

<u>Fusion Curve of n-C<sub>21</sub>H<sub>44</sub></u>		<u>Fusion Curve of n-C<sub>23</sub>H<sub>48</sub></u>	
50 Mol % n-C <sub>21</sub> H <sub>44</sub>	32.6 C	25 Mol % n-C <sub>23</sub> H <sub>48</sub>	33.5 C
65 " " "	35.5	50 " " "	40.3
75 " " "	37.1	75 " " "	44.4
		90 " " "	46.3

The same heat of fusion, that which gave the stable modification at lower temperatures, was taken each time. This amounted to 16,900 cal./mol for n-C<sub>21</sub>H<sub>44</sub> and 19,375 cal./mol for n-C<sub>23</sub>H<sub>48</sub>. In Graph XXIII, the calculated fusion curve is drawn as a T-x figure.

It is to be concluded that the end melting point does not agree generally with the calculated value. As an end melting point of a mixture of 50 mol per cent n-C<sub>21</sub>H<sub>44</sub> and 50 mol per cent n-C<sub>23</sub>H<sub>48</sub>, 44.4 C was found experimentally, and likewise a value of 42.2 C was found as the end melting point of a mixture of 80 mol per cent n-C<sub>21</sub>H<sub>44</sub> and 20 mol per cent n-C<sub>23</sub>H<sub>48</sub>.

From the poor conformity of the observed points with those calculated in the T-x figure, the assumption stating that the two components form a eutetic is proved to be incorrect.

Since information has been published that the components form mixed crystals, a calculation must be made as to where the beginning and end melting points are. Also, it is hereby assumed that no heat of mixing occurs between the paraffins. 2572

The following relation then results:

$$\ln \frac{a_1 p_1}{a_1 p_1 + a_2 p_2} = \frac{1}{y_1} = \frac{Q_1}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \quad (1)$$

Then it follows that :

$$y_1 = \frac{(1-p_1)a_1}{(1-p_1)a_1 + (1-p_2)a_2} \quad (2)$$

$a_1$  and  $a_2$  = the mol fraction of the hydrocarbon

$a_1 p_1$ ;  $a_2 p_2$  = the liquid part at a given temperature

$y_1$ ;  $y_2$  = the composition of the solid paraffin

$Q_1$ ;  $Q_2$  = the molecular heat of fusion of the first and second components, respectively



$T_1$ ;  $T_2$  = the melting point of the first and second components, respectively.

In case the paraffin crystallizes out immediately at the beginning the  $p_1 = 1$  and  $p_2 = 1$ .

Equation (1), in this case, is transposed into:

$$\ln a_1 \frac{1}{y_1} = \frac{Q}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \quad \text{of}$$

$$\frac{Q_1 \left( \frac{1}{T} - \frac{1}{T_1} \right)}{R} \quad (3)$$

$$y_1 = a_1 e$$

For the solid phase it results, upon crystallization, that  $y_1 + y_2 = 1$ . Thus, it follows, in connection with equation (3) that:

$$a_1 e \frac{Q_1}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) + a_2 e \frac{Q_2}{R} \left( \frac{1}{T} - \frac{1}{T_2} \right) = 1 \quad (4)$$

For a mixture of 50 mol per cent  $n\text{-C}_{21}\text{H}_{44}$  and 50 mol per cent  $n\text{-C}_{25}\text{H}_{48}$ , it would be thus:

$$0.5e \frac{16900}{1.986} \left( \frac{1}{T} - 0.003191 \right) + 0.5e \frac{19375}{1.986} \left( \frac{1}{T} - 0.003121 \right) = 1 \quad (4)$$

The solving of the value for  $T$  in the simplest manner from these equations is accomplished by calculating the sums of the values of the e-powers for different values of  $T$ . It is found, for example:

Temp. in C	$\frac{1}{T}$ abs.	Sum of the e-Powers
43	0.003165	2.338
44	0.003155	2.129
44.5	0.003150	2.053
45	0.003145	1.940
46	0.003135	1.767
47	0.003125	1.610

If one then draws the sum of the e-powers as a function of the temperature, the temperature can be read off where the sums are equal to two. These last values correspond then to equation (4). A temperature of 44.7 C is found, which is the beginning of the crystallization of the first trace of paraffin.

In a similar manner, the temperature at which the entire mass completely solidifies can be calculated. The following relation results:

$$0.5e - \frac{16900}{1.9686} \left( \frac{1}{T} - 0.003191 \right) \quad \dagger$$

$$0.5e - \frac{19375}{1.9686} \left( \frac{1}{T} - 0.003121 \right) = 1 \quad (5)$$

From this method it is found that the mixture solidifies completely at a temperature of 43.6 C.

Experimentally, 44.4 and 43.1 C, respectively, was found for this temperature. This agreement can be designated as satisfactory. By these formations of mixed crystals, enough of the correct compound can never be expected to crystallize. Greater or smaller deviation occurs according to the more or less faster cooling.

Using this method, we have calculated the theoretical values to be expected for a mixture of 80 mol per cent  $n\text{-C}_{21}\text{H}_{44}$  and 20 mol per cent  $n\text{-C}_{23}\text{H}_{48}$ .

For the temperature at which the crystallization began, 42.4 C 2574 was calculated and 42.2 C was found experimentally. For the temperature at which the entire mass solidified, 41.6 was found both experimentally and by calculations. The conformity, in this case, is recognized as being good.

From the collective data, it follows that the two hydrocarbons,  $n\text{-C}_{21}\text{H}_{44}$  and  $n\text{-C}_{23}\text{H}_{48}$  together form mixed crystals.

Also, from a temperature-time curve, which is made from an investigation of these mixtures that were combined in a silver vessel that can be sealed, it is evident that these two hydrocarbons form a row of mixed crystals. One can also see from these temperature-time curves that if the transition point in the mixture is lowered considerably, the transition stretch lies between 25 and 26 C while the transition point of pure  $n\text{-C}_{21}\text{H}_{44}$  is 32.8 and that of pure  $n\text{-C}_{23}\text{H}_{48}$  is 40.6.

As the T-x figure was not further investigated, it would be interesting to assemble data concerning it.

## 2. The System of n-Heneicosane and n-Hentriacontane

The ideal fusion diagrams of the systems were calculated again by the recognized equation of Clapyron. The following values were found (for the concentration and temperature) at which the first traces of solid material should appear.

2 Mol %	$n\text{-C}_{31}\text{H}_{64}$	34.9 C	50 Mol %	$n\text{-C}_{31}\text{H}_{64}$	61.1 C
5 " "	"	42.0	65 " "	"	63.4
15 " "	"	50.8	75 " "	"	64.7
25 " "	"	55.1	95 " "	"	66.8
40 " "	"	59.1			

The values found by thermal analysis for the heat of fusion were, namely, 57.7 cal./g; therefore, 57.7 cal./mol.

Simultaneously the fusion curve for  $n\text{-C}_{21}\text{H}_{44}$  was calculated and the following found: at 85 mol per cent, 38.5 C; at 75 mol per cent, 37.1; at 60 mol per cent, 34.6; and at 50 mol per cent, 32.6. The specific total heat of fusion was noted as 57.1 cal./g, therefore 57.1 cal./mol. A graphical representation of all this information is given in Graph XXIV; one sees from this that for a concentration of 4 mol  $\text{C}_{31}\text{H}_{64}$  a eutetic occurs at a temperature of 40 C. The total heat of fusion will always be used at the line of the fusion curve.

The values found and calculated for the freezing points of several 2575 mixtures are as follows.

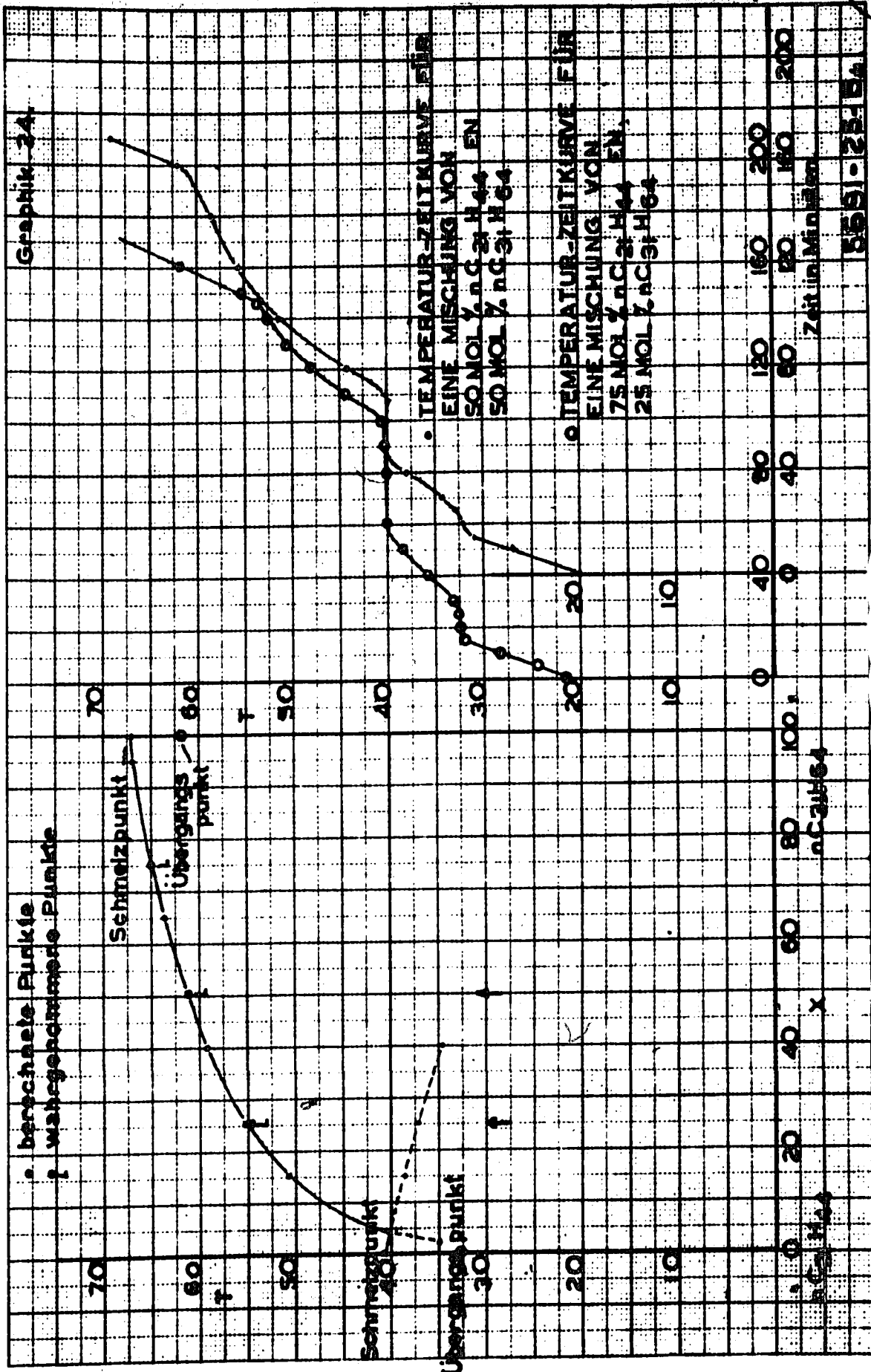
				<u>Found</u>	<u>Calculated</u>
25	Mol %	$n\text{-C}_{31}\text{H}_{64}$	‡	54.6 C	55.1 C
75	" "	$n\text{-C}_{21}\text{H}_{44}$			
50	Mol %	$n\text{-C}_{31}\text{H}_{64}$	‡	61.0	61.1
50	Mol %	$n\text{-C}_{21}\text{H}_{44}$			
75	Mol %	$n\text{-C}_{31}\text{H}_{64}$	‡	64.8	64.7
25	Mol %	$n\text{-C}_{21}\text{H}_{44}$			

The values found and calculated seemed to agree favorably. The components behaved ideally concerning the body of their fusion curves; the presence of a eutetic was very plausible. Also, the course of the temperature-time curve of the mixture of 75 mol per cent  $n\text{-C}_{21}\text{H}_{44}$  and 25 mol per cent  $n\text{-C}_{31}\text{H}_{64}$  and of 50 mol per cent  $n\text{-C}_{21}\text{H}_{44}$  and 50 mol per cent  $n\text{-C}_{31}\text{H}_{64}$  corresponded to the T-x figure planned. A plateau of constant temperature is observed at the eutetic temperature of 40 C. Then the temperature rises slowly up to the point at which the last trace of solid material disappears. At this point, the temperature again undergoes a sharp rise, since without exception the liquid phase warms it up. The transition point of  $n\text{-C}_{21}\text{H}_{44}$  in the mixture will be observed as the same as that in the pure component. It is therefore not probable that a limited mixing occurs in the solid phase. Should this be the case, then an influence, generally, on the transition point by mixing with the second component can be expected.

### 5. The System of $n\text{-Tetracosane}$ and 13-Methylpentacosane

The fusion curves were determined for these systems as in the foregoing cases. The first trace of solid material appeared as given at the temperatures and concentrations appearing below

5	Mol %	$n\text{-C}_{24}\text{H}_{50}$	23.1 C	60	Mol %	$n\text{-C}_{24}\text{H}_{50}$	45.7 C
15	" "	"	32.7	75	" "	"	47.9
25	" "	"	37.4	85	" "	"	49.2
40	" "	"	41.8	95	" "	"	50.3
50	" "	"	43.9				



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In the same way the following values were found for the calculated fusion curve of 13-methylpentacosane.

25 Mol %	$C_{26}H_{54}$	14.9 C	60 Mol %	$C_{26}H_{54}$	23.6 C
50 " "	" "	21.8	75 Mol "	" "	25.9

The total heat of fusion for the normal hydrocarbon  $C_{24}H_{50}$  of 2577 60.8 cal./g, or  $338 \times 60.8 = 20550$  cal./mol, was used; a value was used as the heat of fusion for 13-methylpentacosane of 46.7 cal./g, or  $366 \times 46.7 = 17092$  cal./mol. In Graph XXV the calculated graphical curve is represented. On the basis of this curve, a eutetic can be expected at a temperature of 28 C, while the eutetic combination lies at 8.5 mol per cent tetracosane and, therefore, at 91.5 mol per cent 13-methylpentacosane.

A mixture with a composition of 50 mol per cent tetracosane and 50 mol per cent 13-methylpentacosane was then investigated. This showed a beginning separation of solid material at 43.5 C, while the calculated value was 43.9.

The temperature-time curves for these mixtures correspond to the T-x figures drawn in Graph XXV. The temperature remains at a eutetic constant, increases slowly through the melting range, and increases, except at 43.5 C, even until the solid material has disappeared.

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