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UNIVERSITY OF TARTU, ESTONIA

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BULLETIN No. 2

November 1930

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PHYSICAL PROPERTIES OF  
ESTONIAN SHALE OILS

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P. N. KOGERMAN AND A. KÕLL

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BULLETIN BY THE OIL SHALE RESEARCH LABORATORY



## Physical Properties of Estonian Shale Oils

By

P. N. Kogerman and A. Kõll

The crude Estonian shale oil differs in many respects from well petroleum, although well petroleum itself varies in composition from field to field. The shale oil might be classified as an asphalt base oil, but because of its fairly high contents of phenols it stands about midway between typical asphalt base oils and low-temperature lignite and coal tars. The difference in chemical composition affects to a certain extent the physical properties of the oil. The purpose of the present research was to help the refinery engineer in his calculations, by supplying him with reliable data.

The following physical properties of the crude shale oil and its fractions have been determined:

- (1) specific gravity;
- (2) viscosity;
- (3) surface tension;
- (4) thermal properties:
  - (i) coefficient of expansion;
  - (ii) specific heat;and (iii) heat of vaporisation.

The electrical properties, *i. e.* dielectric constants of neutral oils, were determined by V. Koern, and have been published in this Journal. (Vol. XXXV, 3—4, 1928).

### Experimental

A freshly distilled sample of Kohtla shale oil was used for the determination of physical properties.

The crude oil is a dark-brown liquid with a green fluorescence and a characteristic odour.

The sample used for the experiment contained 1.19% of moisture; its sp. gravity was 1.008 at 18° C; flash point (Martens-Pensky), 91°, and viscosity (Engler) 6.4 at 50°.



The fractionation of the oil was carried out in a 5 litre copper flask, provided with still head, 26 cm in height. To avoid the cracking of the oil at higher temperatures, a reduced pressure, 50 mm Hg, was maintained in the system during distillation. The rate of distillation was about 2 drops per sec. Table I shows the particulars of fractionation. The first fraction up to 150° contained 36.0 g or 1.17% of water. The fractions were dried and filtered.

Table I

Fraction up to 150°	42.5 g	or 1.38%
150°—175°	9.0 "	" 0.29%
175°—200°	15.0 "	" 0.49%
200°—225°	35.5 "	" 1.17%
225°—250°	133.5 "	" 4.42%
250°—275°	166.5 "	" 5.51%
275°—300°	225.0 "	" 7.45%
Total up to 300°	20.71%	

### Specific Gravity and Coefficient of Expansion

A. Specific gravities were determined by means of a pycnometer and a Mohr's balance. For maintaining a constant temperature a water thermostat was used. The particulars of determination are given in Table II and Graph I (Fig. 1) below. It is seen from the graph that the specific gravities of the oils are nearly linear functions of the temperature.

Table II

#### Specific Gravities at Various Temperatures

Temperature	Specific gravities of fractions							Crude oils	
	Up to 150°	150°—175°	175°—200°	200°—225°	225°—250°	250°—275°	275°—300°	From Kohtla retort	From Davidson ret.
20°	0.8204	0.8375	0.8459	0.8582	0.8770	0.8977	0.9257	0.9915	0.9376
30°	0.8126	0.8298	0.8382	0.8507	0.8694	0.8905	0.9187	0.9844	0.9288
40°	0.8049	0.8220	0.8303	0.8430	0.8620	0.8830	0.9116	0.9776	0.9218
50°	0.7968	0.8139	0.8230	0.8356	0.8548	0.8758	0.9047	0.9706	0.9148
60°	0.7896	0.8066	0.8149	0.8280	0.8480	0.8694	0.8980	0.9627	0.9061
70°	—	0.7987	0.8074	0.8212	0.8403	0.8620	0.8910	0.9555	0.8993

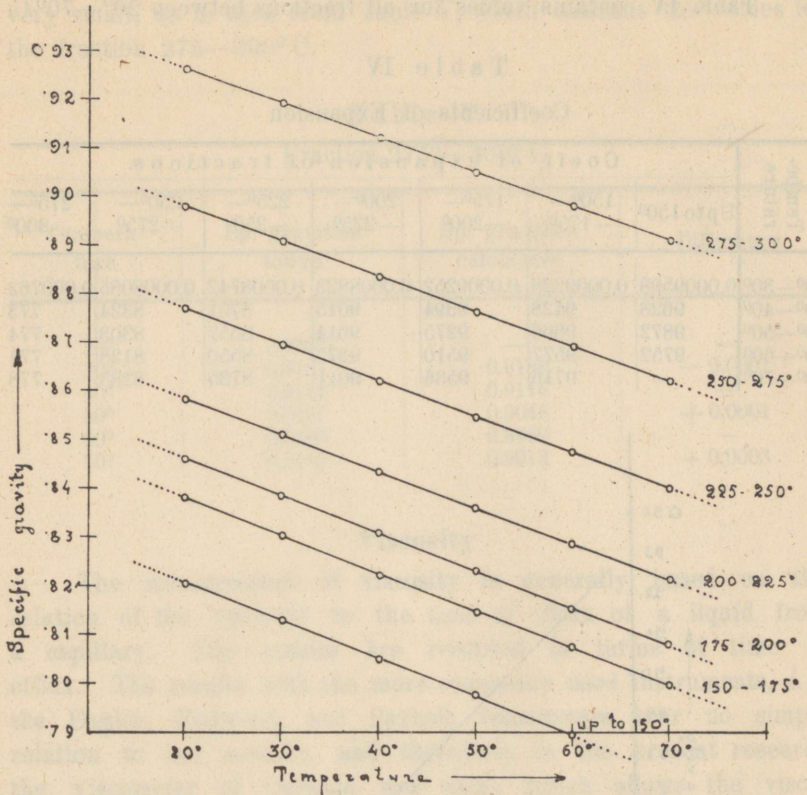


Figure 1.

B. The coefficients of expansion were calculated from the equation

$$a = \frac{a - b}{b(t' - t)} \dots (1)$$

where  $a$  and  $b$  are sp. gravities corresponding to temp.  $t'$  and  $t$ .

The calculated mean values are given in Table III below:

Table III  
Mean Coefficients of Expansion

Fractions	Sp. gravities at 20° C	Mean coeff. of expansion
Up to 150°	0.8204	0.0009712
150°-175°	0.8375	0.0009523
175°-200°	0.8459	0.0009393
200°-225°	0.8582	0.0009027
225°-250°	0.8770	0.0008677
250°-275°	0.8977	0.0008226
275°-300°	0.9257	0.0007716



Table IV contains values for all fractions between 20°—70° C.

Table IV  
Coefficients of Expansion

Temperature	Coeff. of expansion of fractions.						
	Upto 150°	150°— —175°	175°— —200°	200°— —225°	225°— —250°	250°— —275°	275°— —300°
20°—30°	0.0009598	0.0009228	0.0009252	0.0008823	0.0008742	0.0008085	0.000762
20°—40°	9628	9428	9394	9015	8701	8324	773
20°—50°	9872	9666	9275	9014	8657	8303	774
20°—60°	9752	9577	9510	9275	8550	8138	771
20°—70°	—	9716	9536	9011	8735	8283	778

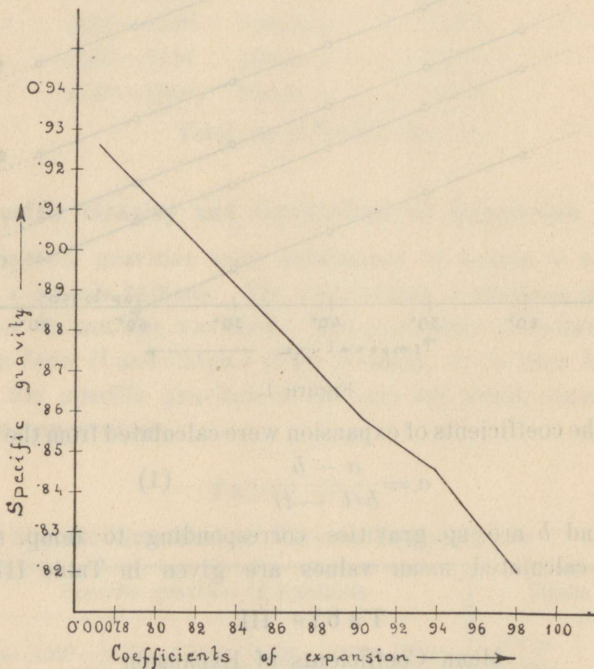


Figure 2.

From the coefficients of expansion one can calculate the values of specific gravities by solving the equation (1) with respect to  $b$ :

$$b = \frac{a}{\alpha(t' - t) + 1} \dots (2)$$

The difference between the observed and the calculated values is



very small, as is seen from Table V, which contains the values for the fraction 275—300° C.

Table V  
Fraction 275°—300° C

Temperature	Sp. gravities found	Sp. gravities calculated	Difference
20°	0.9257	—	—
30°	0.9187	0.9186	— 0.0001
40°	0.9116	0.9116	—
50°	0.9047	0.9048	+ 0.0001
60°	0.8980	0.8980	—
70°	0.8910	0.8913	+ 0.0003

### Viscosity

The measurement of viscosity is generally based on the relation of the viscosity to the time of efflux of a liquid from a capillary. The results are recorded in terms of time of efflux. The results with the more commonly used instruments, *i. e.* the Engler, Redwood, and Saybolt viscometers, bear no simple relation to one another, and therefore, in the present research the viscometer of Ostwald was used, which allows the viscosity to be recorded in "absolute units". Pure distilled water was used as the standard liquid; its coefficient of viscosity  $[\eta]$  equals almost exactly 0.01 at 20.2° C (one centipoise), and density = 0.9982.

For regulating the temperature the water thermostat was used as before.

The values for  $\eta$  were calculated by means of the equation

$$\eta : \eta_0 = \frac{st}{s_0 t_0}, \quad \eta_0, s_0 \text{ and } t_0 \text{ being values of water.}$$

### Blank experiment with water

With the viscometer 5 cc. of water at 20.2° C showed the following times of transpiration: 84.3; 84.4; 84.4; 84.4 secs. Mean value 84.4 secs.

## Fraction up to 150° C

Table VI

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	103.3; 102.8; 103.3; 102.5	102.8	0.010011
30°	90.0; 90.0; 90.0;	90.0	0.008681
40°	79.8; 79.8; 79.8;	79.8	0.007624
50°	72.5; 72.5; 72.5;	72.5	0.006857
60°	65.0; 65.0; 65.0;	65.0	0.006092
70°	— — —	—	—

## Fraction 150°—175° C

Table VII

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	114.1; 114.5; 113.0; 114.5	114.0	0.011300
30°	100.7; 99.6; 100.2; 101.0	100.4	0.009889
40°	87.7; 87.9; 87.5;	87.7	0.008557
50°	78.0; 78.2; 78.1;	78.1	0.007545
60°	71.5; 71.0; 70.0; 71.5	71.0	0.006798
70°	63.5; 62.5; 63.0;	63.0	0.005973

## Fraction 175°—200° C

Table VIII

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	129.6; 129.3; 129.9	129.6	0.013013
30°	111.1; 110.7; 110.9	110.9	0.011033
40°	96.0; 96.0; 96.0	96.0	0.009461
50°	85.2; 85.6; 85.6	85.4	0.008343
60°	76.0; 75.5; 75.9; 75.9	75.8	0.007332
70°	67.7; 68.9; 68.0; 68.3	68.0	0.006517



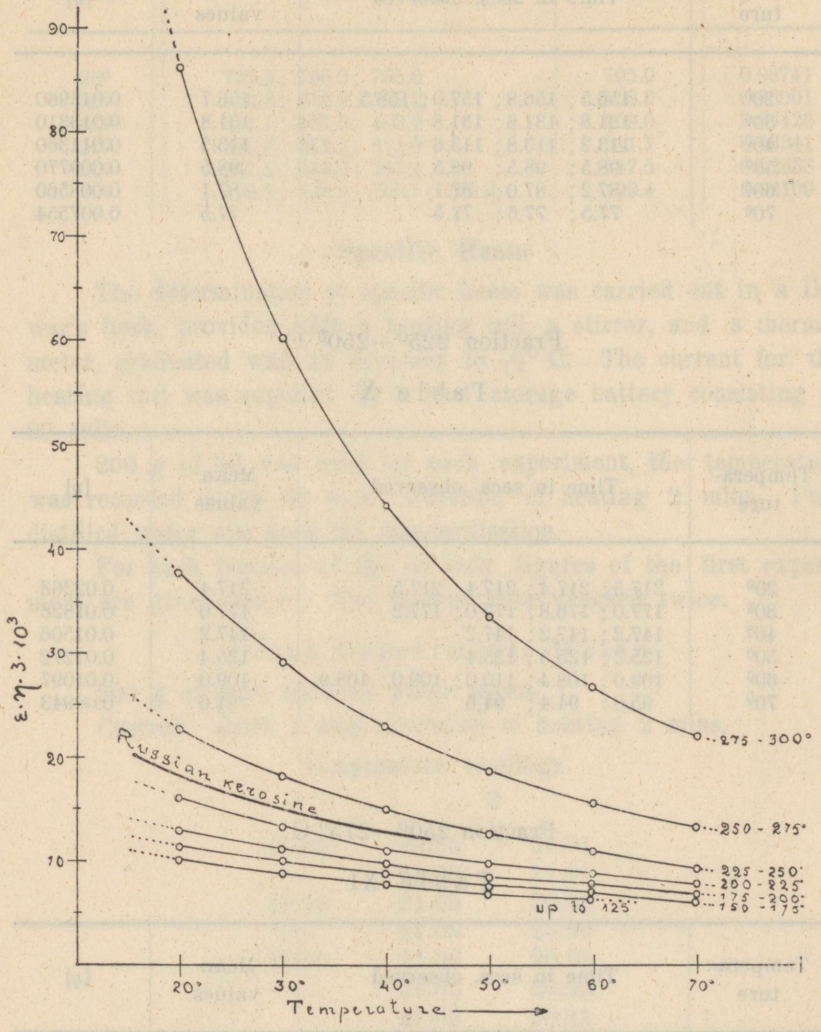


Figure 3.



## Fraction 200°—225° C

Table IX

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	156.5; 156.8; 157.0; 156.5	156.7	0.015960
30°	131.8; 131.8; 131.8	131.8	0.013310
40°	113.2; 113.8; 113.6	113.5	0.011360
50°	98.5; 98.5; 98.5	98.5	0.009770
60°	87.2; 87.0; 87.1	87.1	0.008560
70°	77.5; 77.6; 77.5	77.5	0.007554

## Fraction 225°—250° C

Table X

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	217.3; 217.4; 217.4; 217.5	217.4	0.02263
30°	177.0; 176.8; 177.0; 177.2	177.0	0.01826
40°	147.2; 147.2; 147.2	147.2	0.01506
50°	125.2; 125.5; 125.4	125.4	0.01272
60°	109.0; 108.4; 110.0; 109.0; 108.9	109.0	0.01097
70°	95.0; 94.4; 94.6	94.6	0.00943

## Fraction 250°—275° C

Table XI

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	356.8; 356.4; 356.0; 356.8	356.5	0.03799
30°	276.6; 276.6; 276.4; 276.8	276.6	0.02924
40°	219.6; 219.8; 219.7	219.7	0.02303
50°	178.3; 178.4; 178.3	178.3	0.01853
60°	150.5; 150.8; 150.6	150.6	0.01554
70°	128.4; 129.0; 129.5	129.0	0.01320

## Fraction 275°—300° C

Table XII

Temperature	Time in secs. observed	Mean values	$[\eta]$
20°	795.5; 796.0; 795.0	795.0	0.08741
30°	558.6; 558.9; 558.2	558.6	0.06091
40°	411.1; 407.5; 409.0	409.0	0.04426
50°	310.2; 312.2; 311.0	311.1	0.03341
60°	247.2; 248.0; 247.4	247.5	0.02638
70°	198.8; 198.8; 200.5; 199.8	199.4	0.02109

## Specific Heats

The determination of specific heats was carried out in a Dewar's flask, provided with a heating coil, a stirrer, and a thermometer, graduated with an accuracy to  $\frac{1}{10}^{\circ}$  C. The current for the heating coil was supplied by a lead storage battery consisting of 20 cells.

200 g of oil was used for each experiment, the temperature was recorded every 30 secs. Duration of heating 2 mins. Pure distilled water was used for standardisation.

For each fraction of the oil only figures of the first experiment are given below. The figures were checked twice.

## Blank Experiment: Water

200 g of pure distilled water taken.

Current: about 1 amp. Duration of heating 2 mins.

## Temperature readings

1	2	
18.85	20.85	21.01
—	21.00	21.00
18.83	21.05	20.98
—	21.08	20.96
18.80	21.08	20.95
	21.06	20.93
	21.05	20.91
	21.03	20.90

I Exp. Rise of temperature interpolated 2.45° C

II " " " " " 2.425° C

III " " " " " 2.415° C

Mean value 2.426° C



## Crude Oil

200 g taken. Conditions of experiment same as in case of water.

	1	2	
	20.70	22.10	24.67
	—	23.30	24.71
	20.65	23.70	24.75
	—	23.85	24.75
	20.59	24.10	24.75
		24.40	24.68
		24.60	24.66
		24.65	24.63

I Exp. Rise of temperature interpolated 4.75° C

II " " " " " 4.85° C

III " " " " " 4.82° C

Mean value 4.806° C

$$\text{Specific heat} = \frac{2.426}{4.806} = 0.504$$

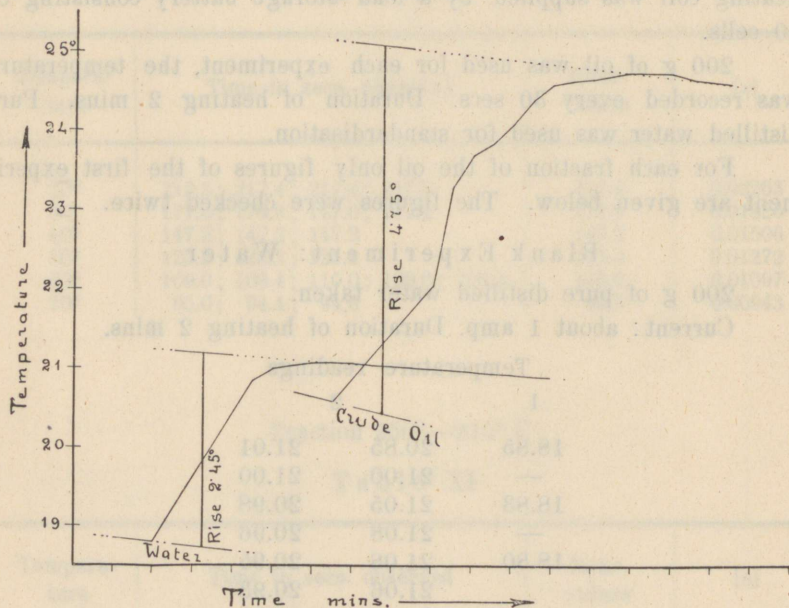


Figure 4.

Fraction up to 150°

Blank experiment with water in this case showed the mean rise 2.31° C. (This experiment was carried out at the end of the other series of experiments).



	1		2	
	14.94	18.20	18.89	18.71
	—	18.70	18.86	18.69
	14.94	18.80	18.84	
	—	18.90	—	
	14.94	18.95	18.80	
		18.94	18.76	
		18.91	—	

I	Exp.	Rise of temperature interpolated	4.20° C
II	"	"	4.16° C
III	"	"	4.18° C
		Mean value	4.18° C

$$\text{Specific heat} = \frac{2.31}{4.18} = 0.552$$

Fraction 150°—200°

	1		2	
	16.55	19.70	20.58	20.36
	—	20.30	—	—
	16.55	20.49	20.53	20.31
	—	—	—	—
	16.55	20.55	20.48	
		—	—	
		20.60	20.44	
		—	20.40	

I	Exp.	Rise of temperature interpolated	4.21° C
II	"	"	4.21° C

$$\text{Specific heat} = \frac{2.31}{4.21} = 0.548$$

Fraction 200°—225°

	1		2	
	18.30	21.80	22.90	
	—	22.50	22.88	
	18.30	22.70	22.86	
	—	22.80	22.84	
	18.30	22.87	22.81	
		22.90	22.80	
		22.90	22.78	

I	Exp.	Rise of temperature interpolated	4.80° C
II	"	"	4.82° C
III	"	"	4.81° C
		Mean value	4.81° C

$$\text{Specific heat} = \frac{2.426}{4.81} = 0.504$$

Fraction 225°—250°

1			2	
18.70	22.00	23.08	22.91	22.70
—	22.50	23.06	22.88	
18.68	22.85	23.01	22.81	
—	23.00	22.98	22.79	
18.60	23.05	22.96	22.74	

I Exp. Rise of temperature interpolated 4.87° C

II " " " " " 4.80° C

III " " " " " 4.78° C

Mean 4.82° C

$$\text{Specific heat} = \frac{2.426}{4.82} = 0.503$$

Fraction 250°—275°

1			2	
17.60	21.10	22.17	22.03	
—	21.90	22.16	22.00	
17.60	22.00	22.15	21.99	
—	22.10	22.11	21.91	
17.60	22.14	22.10	21.90	
	22.17	22.05	21.87	

I Exp. Rise of temperature interpolated 4.85° C

II " " " " " 4.84° C

Mean 4.845° C

$$\text{Specific heat} = \frac{2.426}{4.845} = 0.500$$

Fraction 275°—300°

1			2	
18.15	21.20	22.48	22.37	
—	21.90	22.48	22.34	
18.10	22.25	22.46	22.30	
—	22.40	22.43	22.26	
18.07	22.45	22.40		

I. Exp. Rise of temperature interpolated 4.84° C

II. " " " " " 4.82° C

Mean value 4.83° C

$$\text{Specific heat} = \frac{2.426}{4.83} = 0.502$$



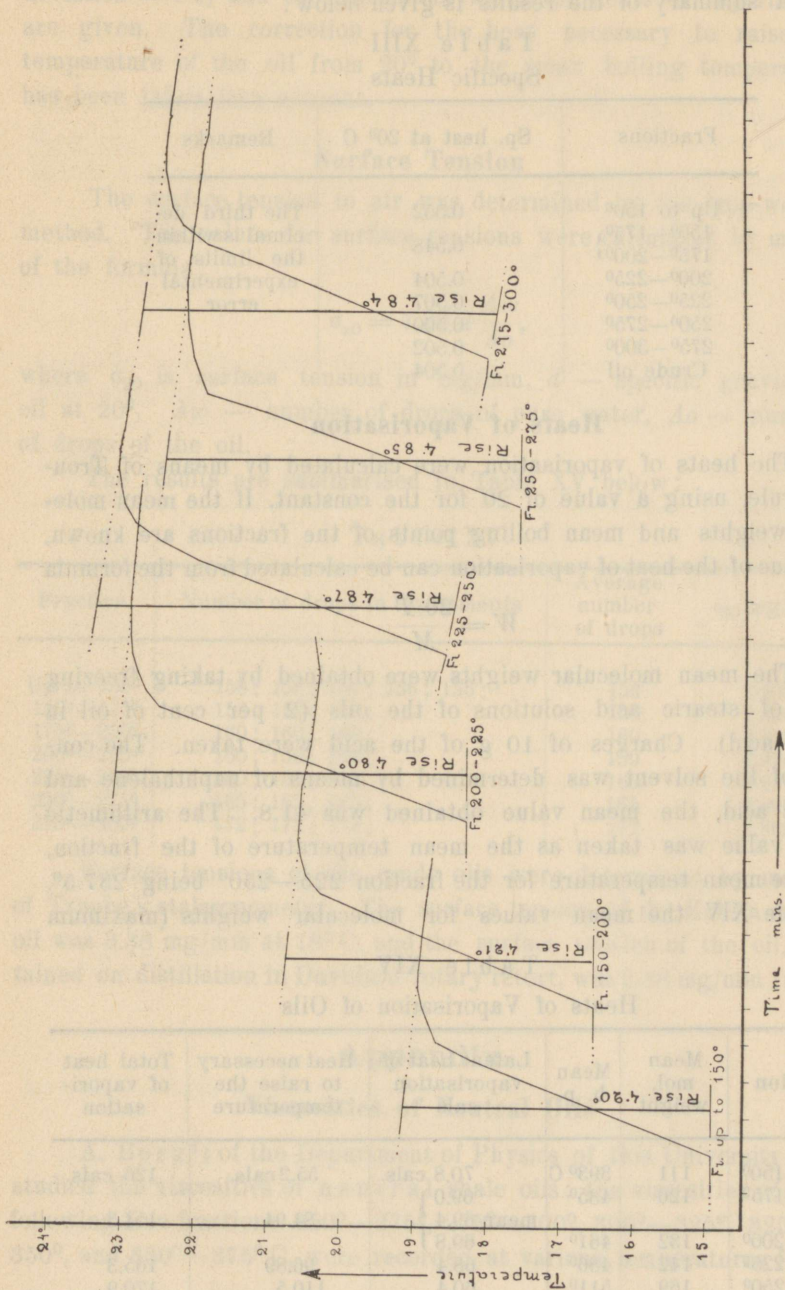


Figure 5.



A summary of the results is given below:

Table XIII  
Specific Heats

Fractions	Sp. heat at 20° C	Remarks
Up to 150°	0.552	The third decimal is within the limits of experimental error
150°—175°	0.548	
175°—200°		
200°—225°	0.504	
225°—250°	0.507	
250°—275°	0.500	
275°—300°	0.502	
Crude oil	0.504	

### Heats of Vaporisation

The heats of vaporisation were calculated by means of Trouton's rule, using a value of 20 for the constant. If the mean molecular weights and mean boiling points of the fractions are known, the value of the heat of vaporisation can be calculated from the formula

$$W = \frac{20 T}{M}$$

The mean molecular weights were obtained by taking freezing points of stearic acid solutions of the oils (2 per cent of oil in stearic acid). Charges of 10 g of the acid were taken. The constant of the solvent was determined by means of naphthalene and benzoic acid, the mean value obtained was 41.8. The arithmetic mean value was taken as the mean temperature of the fraction, *i. e.* the mean temperature for the fraction 225—250° being 237.5°. In Table XIV the mean values for molecular weights (maximum

Table XIV  
Heats of Vaporisation of Oils

Fraction	Mean mol. weight	Mean b. p.	Latent heat of vaporisation calcs	Heat necessary to raise the temperature	Total heat of vaporisation
Up to 150°	111	393° C	70.8 calcs.	55.2 calcs.	126 calcs.
150°—175°	126	435°	69.0		
175°—200°	132	461°	mean 69.4	84.94	154.3
200°—225°	142	486°	69.8		
225°—250°	169	511°	68.4	96.89	165.3
250°—275°	178	536°	60.4	110.5	170.9
275°—300°	199	561°	60.2	121.5	181.7
			56.4	134.5	190.9

deviation  $\pm 4\%$ ) and the calculated values for heats of vaporisation are given. The correction for the heat necessary to raise the temperature of the oil from  $20^{\circ}$  to the mean boiling temperature has been taken into account.

### Surface Tension

The surface tension to air was determined by the drop-weight method. The values for surface tensions were calculated by means of the formula:

$$\sigma_{20} = 7.30 d \frac{Aw}{Ao},$$

where  $\sigma_{20}$  is surface tension in mg/mm,  $d$  — specific gravity of oil at  $20^{\circ}$ .  $Aw$  — number of drops of pure water,  $Ao$  — number of drops of the oil.

The results are summarised in Table XV below:

Table XV

Fraction	Number of drops in experiments	Average number of drops	$\sigma_{20}$ mg/mm
Up to $150^{\circ}$	156; 156; 157; 156; 156;	156	2.802
$150^{\circ}$ — $175^{\circ}$	158; 157; 159;	158	2.824
$175^{\circ}$ — $200^{\circ}$	160; 160; 160;	160	2.818
$200^{\circ}$ — $225^{\circ}$	160; 159; 159;	159	2.876
$225^{\circ}$ — $250^{\circ}$	160; 160; 160;	160	2.931
$250^{\circ}$ — $275^{\circ}$	165; 165; 165;	165	2.899
$275^{\circ}$ — $300^{\circ}$	172; 172; 172;	172	2.868

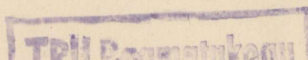
Surface tensions of the crude oils were determined by means of Traube's stalagmometer. The surface tension of the Kohtla crude oil was 3.38 mg/mm at  $18^{\circ}$  C, and the surface tension of the oil, obtained on distillation in Davidson rotary retort, was 2.88 mg/mm  $18^{\circ}$  C.

## Appendix

### Viscosities of Neutral Oils

A. Berg<sup>1)</sup> of the Department of Physics of this University has studied the viscosities of neutral shale oils; the viscosities of the following five fractions  $250^{\circ}$ — $275^{\circ}$ ,  $275^{\circ}$ — $300^{\circ}$ ,  $300^{\circ}$ — $325^{\circ}$ ,  $325^{\circ}$ — $350^{\circ}$ , and  $350^{\circ}$ — $375^{\circ}$  C, were recorded at various temperatures from

1) Unpublished dissertation.





0° to 100° C. A specially designed capillary viscometer was used for the measurements of viscosity. Length of the capillary 16.68 cm, diameter 35.327 mm.

By plotting the observed values of viscosities of each fraction against temperature on a logarithmic scale, straight lines were obtained. The relation between viscosity and temperature might be expressed by the following equation:

$$\eta = \frac{C}{(T + \tau)} n - A,$$

where  $C$  and  $A$  and  $\tau$  are constants.

To suit the equation the calculated values of the constants must be slightly different for each fraction, as is seen from Table XVI.

Table XVI

Fractions	C o n s t a n t s			Time of efflux in secs.*)
	$n$	$A$	$\tau$	
250—275°	1.417	$0.09 \times 10^{-2}$	49°	773 (20°); 513 (50°); 384 (90°)
275—300°	1.452	$0.18 \times 10^{-2}$	47°	802 (19°); 518 (52°); 417 (93°)
300—325°	1.483	$0.25 \times 10^{-2}$	42°	899 (24°); 704 (53°); 490 (93°)
325—350°	1.525	$0.31 \times 10^{-2}$	36°	1237 (22°); 1036 (51°); 554 (91°)
350—375°	1.549	$0.36 \times 10^{-2}$	28°	1866 (18°); 975 (50°); 650 (89°)

\*) Note: The values given are merely illustrations, the observations were recorded at about 16 different temperatures, between 0°—100° for each fraction of the neutral oil.

Viscosities of crude oils in Engler degrees were as follows:

(1) Kohtla crude shale oil  $E_{20^\circ} = 33.2$ ;  $E_{50^\circ} = 1.9$ .

(2) Crude from Davidson retort  $E_{20^\circ} = 3.5$ ;  $E_{50^\circ} = 1.2$ .

### Summary

(1) Physical constants of the crude Estonian shale oil and its seven fractions have been determined.

(2) A close similarity is observed between the constants of the shale oils and those of crude petroleum and its distillates.

(3) The coefficients of expansion are slightly higher than those found in the case of petroleum products.

(4) The values for heats of evaporation of the shale oils are very close to the figures obtained in the case of oils from lignite tars.

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