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MEASUREMENT OF THERMAL CONDUCTIVITIES OF ORGANIC ALIPHATIC LIQUIDS BY AN ABSOLUTE UNSTEADY-STATE METHOD

W. JOBST

Institute of Chemical Engineering and Cyrogenics of the Swiss Federal Institute of Technology, Zürich

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Abstract—Experimental results in the temperature range from $-100°$ to $+200°$C of 43 fluids (*n*-paraffins, *n*-alcohols, *n*-fatty acids, *n*-ketones, *n*-aldehydes and *n*-ethers) are presented. The systematic change of conductivity with temperature (or density) and molecular weight in homologous series is shown.

NOMENCLATURE

A, factor, defined in equations (2) and (4);
B, exponent defined in equations (2) and (3);
n_c, number of carbon atoms in the molecule;
T, temperature [°C];
ρ, density [kg/m³];
ρ_M, molar density [Mol/m³];
k, thermal conductivity [W/m degC],

$$1 \frac{\text{Btu}}{\text{h ft degF}} = 1{\cdot}74 \frac{\text{W}}{\text{m degC}} = 1{\cdot}49 \frac{\text{kcal}}{\text{m h degC}}.$$

INTRODUCTION

IN RECENT years much has been done to improve the existing methods for measuring liquid thermal conductivities within an accuracy of 1 per cent or better. These precision-measurements and their evaluations are time consuming and cover only a comparatively narrow temperature range in most cases. Little has been done in the way of measuring

(a) reliable coefficients of thermal conductivities over a wide temperature range;
(b) homologous series in order to find a regularity within a series and between different homologous series.

Grassmann and Straumann have developed an unsteady-state relative method [1] which is ideally suited for measurement of series over a wide temperature range. This simple and quick relative technique has now been modified to an absolute method, which will be described in detail in a later publication. (As it appears, a similar method has in the meantime been developed independently by Horrocks and McLaughlin [2].) The experimental results are accurate to within 2 per cent. A number of organic compounds, summarized in Table 1, have been measured in the temperature range from $-100°$ to $+200°$C.

Table 1

n_c = number of carbon atoms in the molecule	
7 normal paraffins	n_c = 5 to 12
11 normal alcohols	= 1 to 14
13 normal fatty acids	= 1 to 22
5 normal ketones	= 3 to 9
3 normal aldehydes	= 3 to 5
4 normal ethers	= 4 to 12

Only fluids of the qualities "purum" or "purissimum" were employed for the measurements. To prove the effective purity, the experimental indices of refraction were compared with values from the literature [3]. The deviations were, with few exceptions, of the order of some 0·1 per cent.

Except for the paraffins all tested liquids are polar fluids, which were selected because the

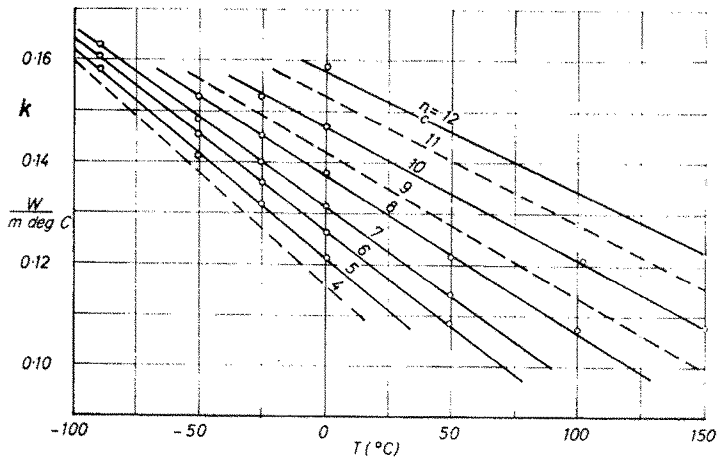

FIG. 1. Thermal conductivity of normal paraffins as a function of temperature. Line for C_4H_{10} extrapolated, for $C_{11}H_{24}$ interpolated.

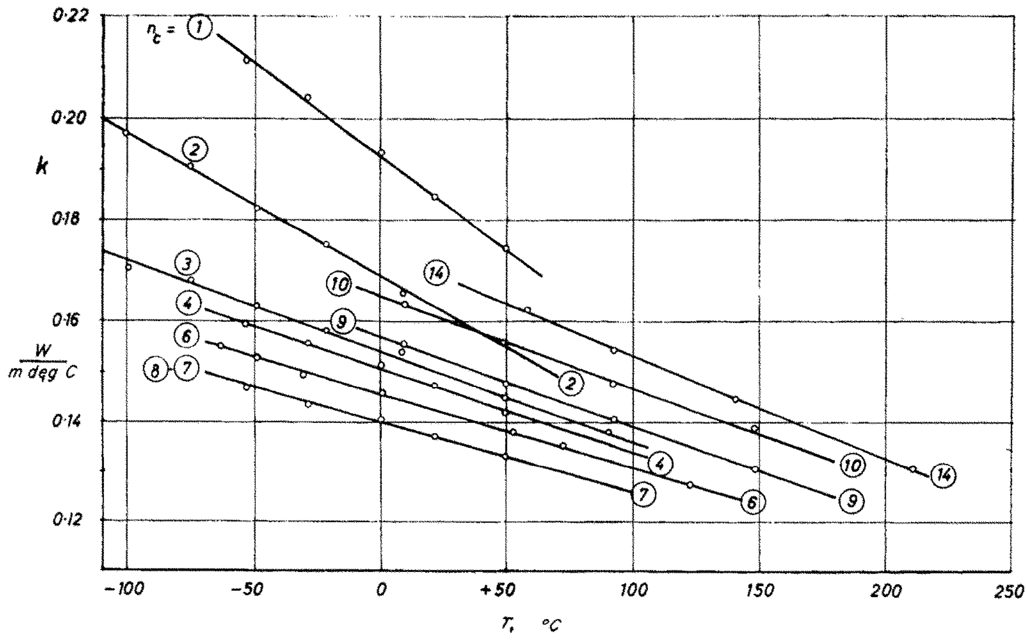

FIG. 2. Thermal conductivity of *n*-alcohols as a function of temperature.

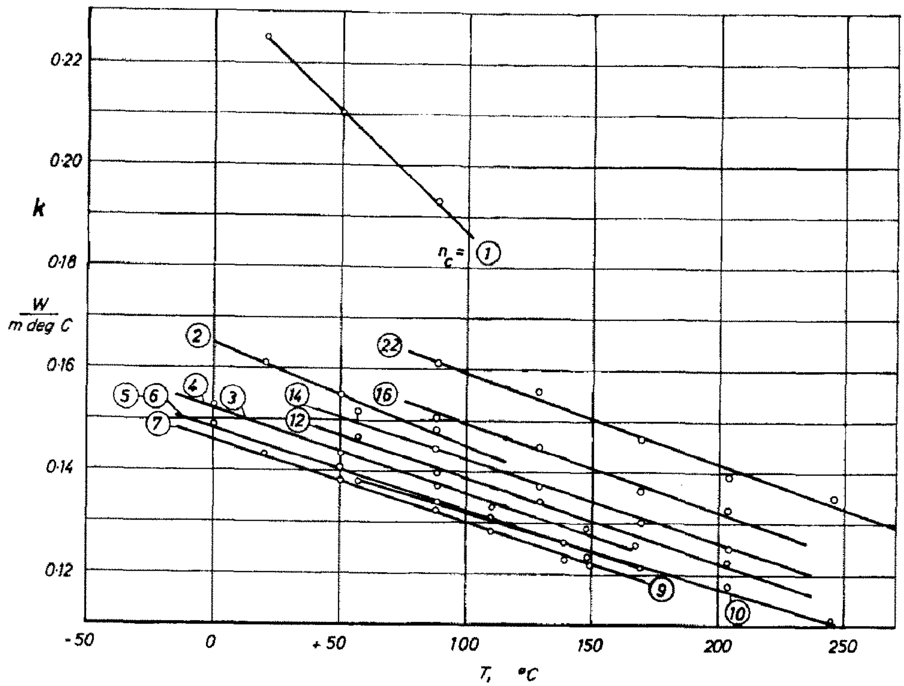

FIG. 3. Thermal conductivity of normal fatty acids as a function of temperature.

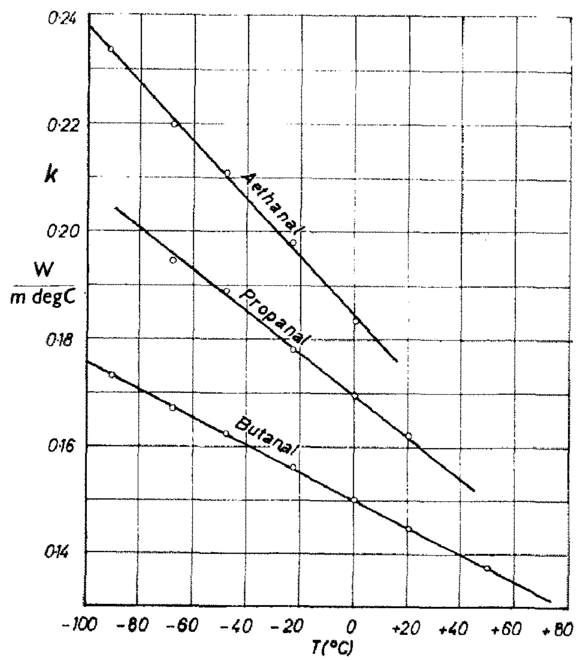

FIG. 4. Thermal conductivity of *n*-aldehydes as a function of temperature.

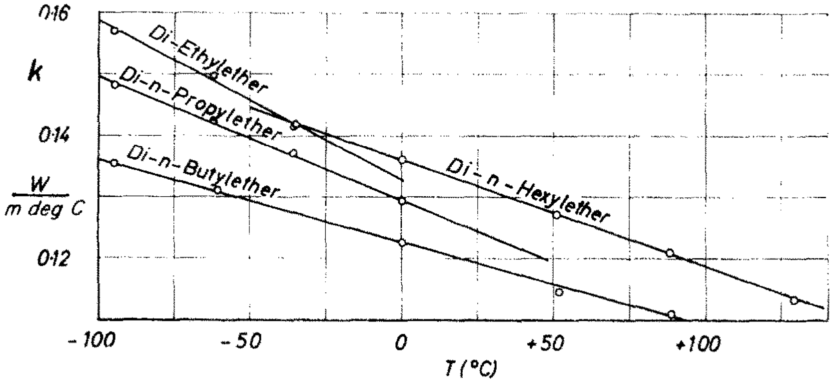

FIG. 5. Thermal conductivity of *n*-ethers as a function of temperature.

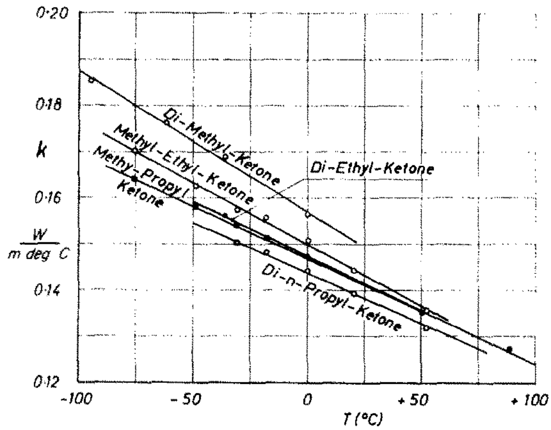

FIG. 6. Thermal conductivity of *n*-ketones as a function of temperature.

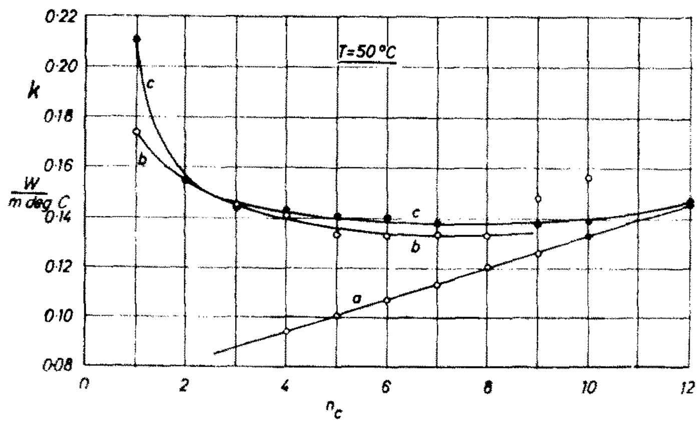

FIG. 7. Thermal conductivity of *n*-paraffins, *n*-alcohols and normal fatty acids at a constant temperature $T = 50°C$.

a = paraffins *b* = alcohols *c* = fatty acids

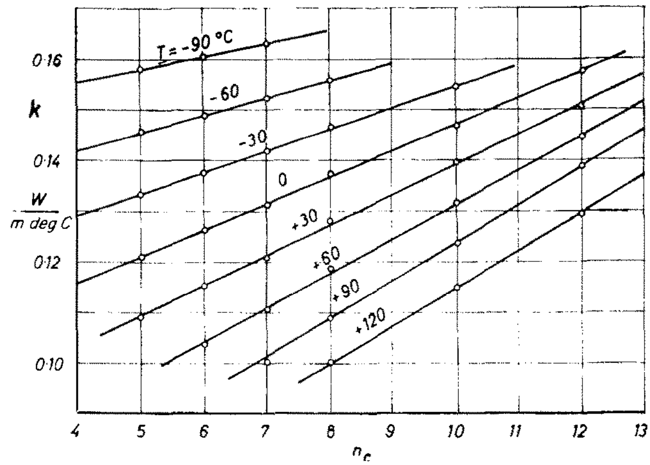

FIG. 8. Thermal conductivity as a function of n_c (number of carbon atoms in the molecule) of normal paraffins at different reference temperatures.

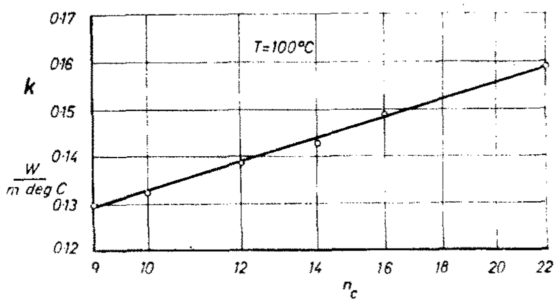

FIG. 9. Thermal conductivity of higher normal fatty acids as a function of n_c.

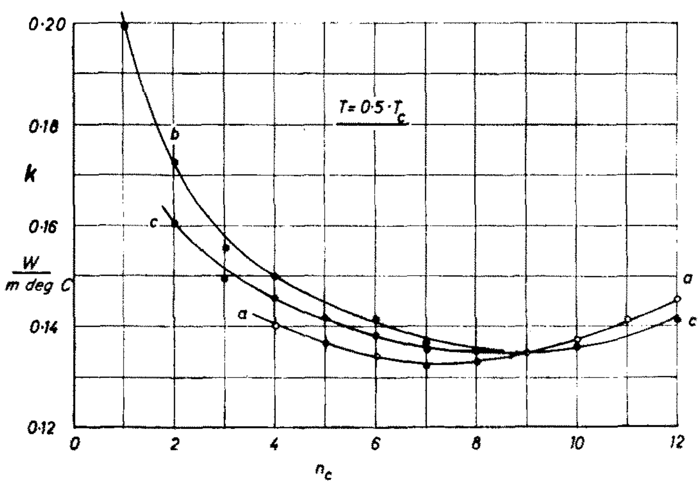

FIG. 10. Thermal conductivity of paraffins, alcohols and fatty acids at a reduced temperature $T_R = 0{\cdot}5$.

a = paraffins b = alcohols c = fatty acids

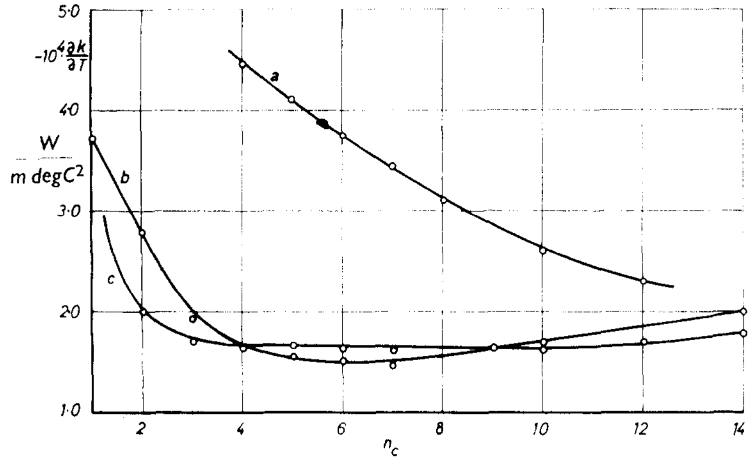

FIG. 11. Comparison of temperature coefficients of paraffins, alcohols and fatty acids.
a = paraffins b = alcohols c = fatty acids

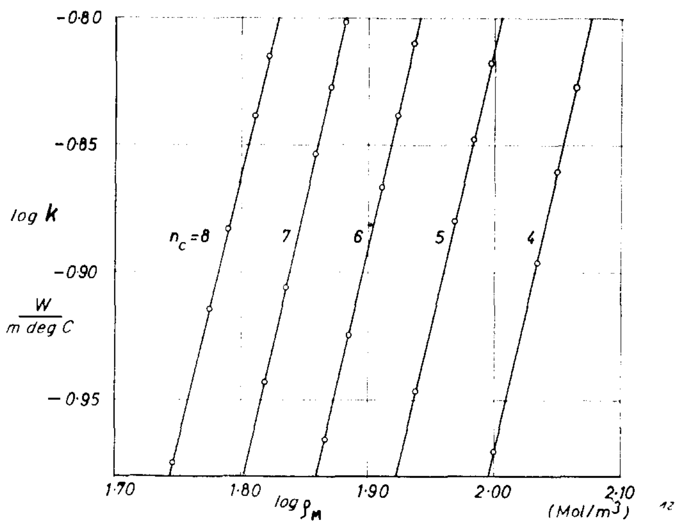

FIG. 12. Exponent B in equation (2) as a function of n_c for normal paraffins.

theoretical prediction of their thermal conductivities is particularly uncertain. The paraffins were included for comparison because their relatively simple unpolar molecules should yield uncomplicated results.

EXPERIMENTAL RESULTS

In Figs. 1 to 6 all of the experimental thermal conductivities are plotted against temperature. A striking fact is the possibility of linear interpolation for all fluids over a wide temperature range. However, these graphs with their great number of straight lines are only suited for a qualitative comparison of the results.

EVALUATION OF RESULTS

Figure 7 presents a clearer survey of the thermal conductivities of paraffins, alcohols and fatty acids for a constant reference temperature, $T = 50°C$.

The linear increase of thermal conductivity with n_c (number of carbon atoms in the molecule) for the n-paraffins is surprising. Alcohols and fatty acids, consisting of small molecules, show a completely different tendency relative to the paraffins. For large molecules all three series show a good agreement, except two alcohols with $n_c = 9$ and 10.

Figure 8 demonstrates the very regular variation of thermal conductivities with n_c for the n-paraffins at different constant temperatures.

Figure 9 corresponds to Fig. 7 and illustrates a proportionality between k and log n_c for the higher fatty acids at $T = 100°C$.

A comparison of the thermal conductivities at constant reference temperatures is not satisfactory because the substances differ greatly in their melting—boiling—and critical temperatures. A more common property for reference is the reduced temperature. In Fig. 10 k is plotted against n_c at a constant reduced temperature $T_R = T/T_c = 0{\cdot}5$. The critical properties of the

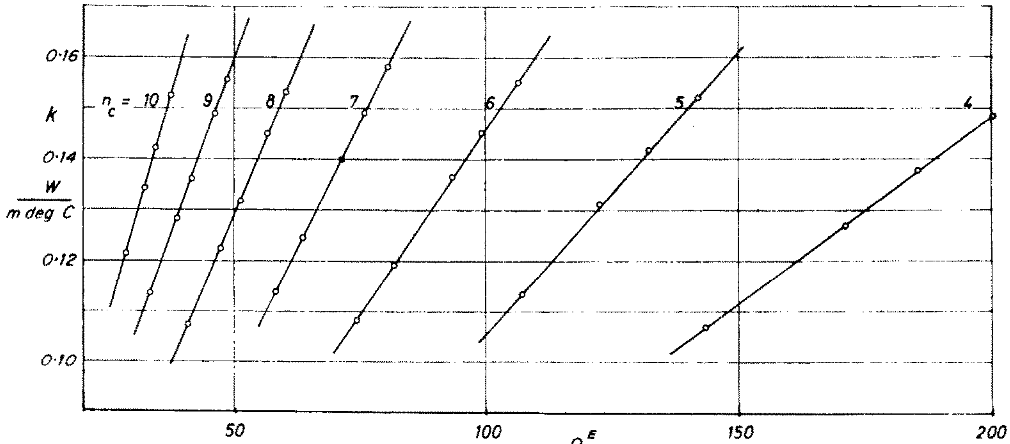

FIG. 13. Invariability of slope $\partial k/\partial(\rho_M{}^B)$ for each fluid under test.

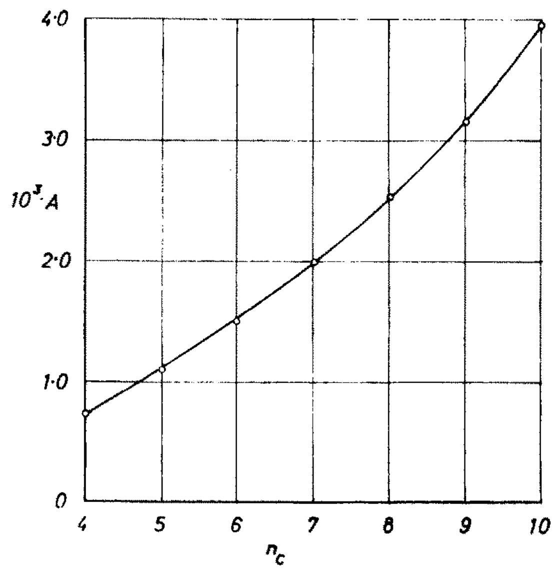

FIG. 14. Variation of A in equations (2) and (4) as a function of n_c.

normal fatty acids were calculated by the method developed by Lydersen [4]. This reduction with critical temperatures leads to a fairly similar behaviour of the three curves.

The temperature coefficients of thermal conductivity are evaluated with good accuracy out of diagrams k against T. Figure 11 demonstrates the great negative temperature coefficient of n-paraffins in comparison to that of polar liquids. The fluids composed of heavy molecules converge toward a limiting value, which is about the same for all three homologous series.

CALCULATIONS FOR n-PARAFFINS

As mentioned above the behaviour of normal paraffins, corresponding to their molecular construction, is especially simple. Thus their temperature coefficients of thermal conductivity depend on the number of carbon atoms in the molecule in a very simple manner:

$$10^4 \partial k/\partial T = -7{\cdot}26 + 4{\cdot}61 \times \log n_c \quad (1)$$

Further inquiries lead to the general equation

$$k = A \cdot \rho_M^B \qquad \rho_M \text{ [mol/m}^3] \quad (2)$$

A and B depend only on the fluid under consideration, ρ_M also on the temperature. Equation (2) transformed yields

$$B = \partial \log k/\partial \log \rho_M \quad (3)$$

Figure 12 demonstrates that the exponent B remains constant for the lower weight paraffins. As checked till now, B will change its numerical value for other homologous series, but remain independent on temperature.

To obtain the values of A the general equation (2) is written as

$$A = \partial k/\partial(\rho_M^B) \quad (4)$$

Figure 13 shows the invariability of the slope for each fluid under test. This means that for the paraffins A is independent of the temperature and related only to n_c.

$$A = 3{\cdot}39 \times 10^{-5}(0{\cdot}700 + n_c)^2 \qquad A \text{ [W(m}^3\text{/mol)}^B\text{/m degC]} \quad (5)$$

Comparison of experimental results and equation (5) in Fig. 14. Further evaluations for the other fluids tested are being established.

ACKNOWLEDGEMENT

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Résumé—On présente des résultats expérimentaux dans la gamme de température entre −100° et +200°C pour 43 fluides (n-paraffines, n-alcools, n-acides gras, n-acétones, n-aldéhydes et n-éthers). On montre la variation systématique de la conductivité avec la température (ou la densité) et le poids moléculaire dans les séries homologues.

Zusammenfassung—Im Temperaturbereich von −100° bis +200°C werden experimentelle Ergebnisse der Wärmeleitfähigkeit von 43 Flüssigkeiten mitgeteilt (n-Paraffine, n-Alkohole, n-Fettsäuren, n-Ketone, n-Aldehyde, n-Aether). Die systematische Änderung der Warmeleitfahigkeit mit der Temperatur (oder der Dichte) und dem Molekulargewicht in homologen Reihen wird gezeigt.

Аннотация—Приводятся экспериментальные данные для 43 жидкостей (нормальные парафины, нормальные спирты, нормальные жидкие кислоты, нормальные кетоны, нормальные альдегиды и нормальные простые эфиры) в температурном диапазное от −100° до +200°C. Показано систематическое изменение теплопроводности в зависимости от температуры (или плотности) и молекулярного веса в гомологических рядах.