OLEFIN-VAPOR CONDUCTIVITIES BELOW 0.1 MPa AT 220-680 K

V. A. Kurbatov and N. A. Nesterov

UDc 563.2.08

A curve has been fitted to measurements on the thermal conductivities of olefin vapors at 220-680 K, which is based on the corresponding-state theory. Measurements have been made on the thermal conductivity of non-1-ene at 303-372 K.

Table 1 collects measurements on the thermal conductivities of olefin vapors at $P \leq 0.1$ MPa, which have been made by many workers over the last 20 years.

The existing theory does not give a relationship for the thermal conductivities of polyatomic olefins, so as measurements have accumulated, curves have been fitted to provide reliable engineering data. For example, in [29], measurements up to 1967 were used with a semiempirical method to give recommended reference data for ethylene at 170-450 K and propylene at 270-450 K with an error of ±4%. In [30], least-squares fitting was applied to various measurements on ethylene (apart from the [8] results, which have the large error of ±5%), and smoothed λ were derived for 273-620 K. In [18], the author used his own measurements with least-squares fitting to obtain smoothed values for ethylene and propylene at 180-500 K and but-1-ene from 300 to 500 K, where the estimated the maximum error was ±1%. The [18] data for but-1-ene below 300 K were obtained by extrapolation.

In [31], the recommended data for ethylene cover the range 180-273 K as derived from [18] or from [30] for 273-620 K. The error in the tabulated data is 1.5% at 273-473 K or 2% for other temperatures. In [31], the available measurements were used in tabulated values, whose error was 2% for propylene at 230-470 K or but-1-ene at 300-500 K, 2-3% for hex-1-ene at 350-620 K, hept-1-ene at 380-670 K, oct-1-ene and non-1-ene at 420-670 K, and 3% for propylene at 420-620 K and dec-1-ene at 470-650 K.

The [18, 29, 31] data for ethylene, propylene, and but-1-ene show discrepancies not exceeding ±2% in the overlapping ranges, apart from the [29] data for ethylene, which are lower than the [31] values at temperatures from 180 to 260 K correspondingly by from 14.4 to 1.2%.

In [26-28], the authors used their own measurements (Table 1) to derive a single equation of Sutherland type, from which they calculated the conductivities from hex-1-ene to pentadec-1-ene over wide temperature ranges [28]. The deviations in the measurements from the fitted values did not exceed ±2% for non-1-ene, dec-1-ene, and undec-1-ene, while the measured λ for hept-1-ene and oct-1-ene were overestimated by 0.3-3.2%.

Table 1 shows that there are no measurements on but-1-ene below 300 K, non-1-ene below 453 K, undec-1-ene below 489 K, and for pentene and members of the homologous series below undecene. Also a Sutherland-type semiempirical equation [26-28] is applicable to the olefin λ beginning with hept-1-ene only above the normal boiling points, while in [31], the fitting equations $\lambda = f(T)$ were not given apart from for ethylene.

We have derived a single curve for the olefins at 220-680 K and $P \leq 0.1$ MPa. Similarity theory implies

$$\lambda/\lambda_{T\,\mathrm{nbp}} = f(\tau), \tag{1}$$

in which $\tau = T/T_{nbp}$ is the reduced tempeature, T_{nbp} is the normal boiling point, and $\lambda_{T_{nbp}}$ is the thermal conductivity at T_{nbp}.

We derived values for $\lambda_{T_{nbp}}$ where T_{nbp} by least-squares processing of the measurements for propylene [11, 18, 21, 29], hex-1-ene [24], hep-1-ene and oct-1-ene [24, 26], non-1-ene

Applied Physics Institute, Belorussian Academy of Sciences, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 57, No. 3, pp. 480-485, September, 1989. Original article submitted March 11, 1988.

 0022-0841/89/5703-1100$12.50

TABLE 1. Measurements on Olefin Thermal Conductivities at $P \leq 0.1$ MPa

Year	Source	Temperature, K	Method	Error, %
		Ethylene		
1913	[1]	202—273	Heated filament	Not stated
1940	[2]	273	»	»
1949	[3]	343	»	»
1951	[4]	314; 340	Coaxial cylinders	±1,0
1953	[5]	303	Heated filament	Not stated
1954	[6]	345; 425	Coaxial cylinders	»
1955	[7]	339	Heated filament	»
1958	[8]	293—523	Coaxial cylinders	±5,0
1962	[9]	591	»	Not stated
1964	[10]	298—473	Heated filament	+1,0
1967	[11]	246—399	Coaxial cylinders	Not stated
1969	[12]	304—373	Heated filament	±1,0
1970	[13]	298—479	»	±1,5—2,0
1971	[14]	193—573	Regular state	±2,0
1971	[15]	200—500		±1,5
1972	[16]	301—618	Coaxial cylinders	
1973	[17]	201—553	Regular state	±2,0
1974	[18]	183—477	Heated filament	±1,0
		Propylene		
1949	[3]	343	Heated filament	Not stated
1953	[5]	303	»	»
1955	[7]	339	»	»
1964	[10]	298—473	»	±1,0
1967	[11]	273—400	Regular state	
1968	[19]	293—633	»	±1,4
1970	[20]	296—641	»	»
1971	[21]	233—573	»	±2,0
1972	[22]	323; 373	Heated filament	±2,0
1974	[18]	185—478	»	±1,0
		But-1-ene		
1960	[23]	297	Heated filament	Not stated
1972	[22]	323; 373	»	±2,0
1974	[18]	301—478	»	±1,0
		Hex-1-ene		
1968	[19]	293—633	Heated filament	±1,4
1988	[24]	305—371	»	±1,3
		Hept-1-ene		
1968	[19]	293—633	Regular state	±1,4
1969	[28]	373—623	»	»
1980	[26]	383—678	Monotone heating	±2,0
1988	[24]	302—369	Heated filament	±1,3
		Oct-1-ene		
1968	[19]	293—633	Regular state	±1,4
1976	[27]	413—673	Monotone hating	±2,0
1980	[25]	418—678	»	»
1988	[24]	304—370	Heated filament	±1,3
		Non-1-ene		
1976	[27]	453—673	Monotone heating	±2,0
1980	[26]	502—677	»	»
		Dec-1-ene		
1976	[27]	473—673	Monotone heating	±2,0
1980	[25]	469—654	»	»
1988	[24]	304—368	Heated filament	±1,3
		Undec-1-ene		
1980	[28]	489—627	Monotone heating	±2,0

Note. The [26] measurements for olefins from nept-1-ene to undec-1-ene have been given graphically in an earlier paper [28].

TABLE 2. Measured Conductivities for Non-1-ene Vapor at 4.5×10^2 Pa in 10^3 W/m·K

T, K	λ	T, K	λ	T, K	λ
302,66	9,81	318,12	10,89	354,42	13,78
302,67	9,83	322,69	11,11	362,49	14,54
303,09	9,84	332,05	11,91	364,29	14,72
304,35	9,93	334,25	12,00	369,93	15,34
310,00	10,30	345,08	12,95	371,78	15,46
313,41	10,50	353,96	13,77		

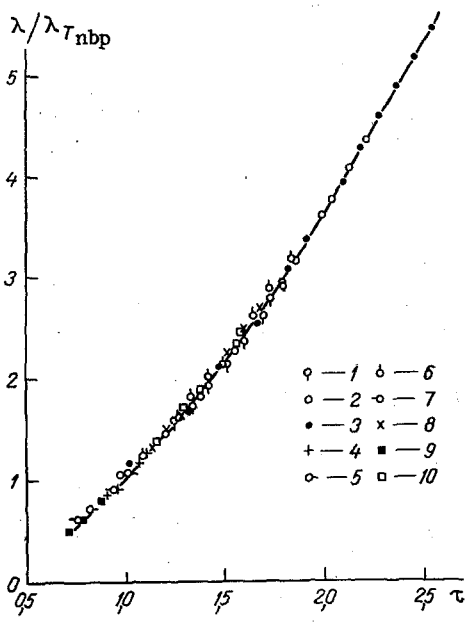

Fig 1. Temperature dependence of the thermal conductivity for olefin vapors in reduced coordinates. Propylene: 1) [11, 29], 2) [18], 3) [21]; hex-1-ene: 4) [24]; hep-1-ene; 5) [24]; 6) [26]; oct-1-ene: 7) [24]; 8) [26]; non-1-ene: 9) our results; 10) [26].

[26], and our measurements (Table 2).* The normal boiling points were taken from [32]. We found that here $\lambda_{T_{nbp}} = f(T_{nbp})$ was linear within the experimental error:

$$\lambda_{T_{nbp}} = (-1{,}0149 + 0{,}0508 T_{nbp}), \quad (2)$$

with T_{nbp} in K and $\lambda_{T_{nbp}}$ in mW/m.K.

In the processing, we neglected the measurements on propylene from [10, 19], hex-1-ene and oct-1-ene in [19], and hept-1-ene in [19, 25] as being insufficiently reliable [24, 31].

Figure 1 shows the data processes via (1). The measurements for the olefins from hex-1-ene to non-1-ene and for propylene fit well on a single curve:

$$\lambda/\lambda_{T_{nbp}} = -0{,}4246 + 0{,}8208\tau + 0.5918\tau^2, \quad (3)$$

which applies for τ = 0.72-2.54. The maximum spread around the curve is due to certain points for propylene and hept-1-ene, where it attains 3%.

From (2) and (3) we get

*The measurements were made with an apparatus based on the absolute heated-filament method [24]. The maximal relative error (0.95 confidence limits) was ±1.8%.

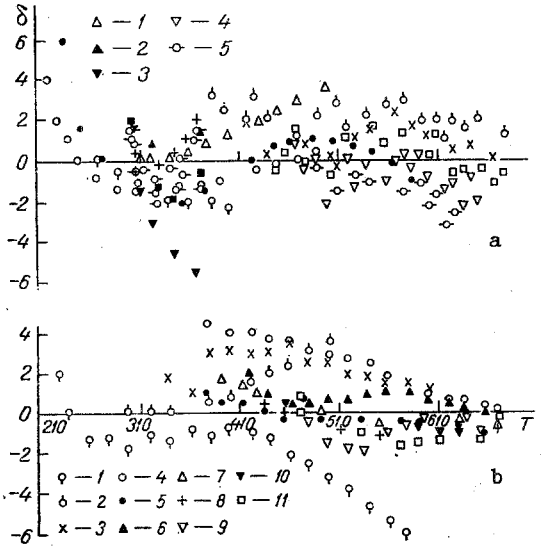

Fig. 2. Deviations in the measurements, recommended reference data [31], and fitted data [28] on the conductivities of olefin vapors from those calculated from (4): a) but-1-ene: 1) [18]; 2) [22]; dec-1-ene: 3) [24]; 4) [26]; undec-1-ene: 5) [26]; other symbols as in Fig. 1; b) 1-3) [31] correspondingly for propylene, but-1-ene, and hex-1-ene; hept-1-ene: 4) [31], 5) [28]; oct-1-ene: 6) [31], 7) [28]; non-1-ene; 8) [28]; dec-1-ene: 9) [31]; 10) [28]; undec-1-ene: 11) [28]. δ, %; T, K.

$$\lambda = (-0.4246 + 0.8208\tau + 0.5918\tau^2)\cdot(-1.0149 + 0.0508T_{nbp}), \quad (4)$$

with T_{nbp} in K and λ in mW/m·K.

The λ_{exp} and the λ_{calc} from (4) agree within 2-3% in most cases, including points not used in the processing (for but-1-ene, dec-1-ene, and undec-1-ene) when expressed as the deviations $\delta = \lambda_{exp} - \lambda_{calc}/\lambda_{calc}\cdot 100\%$ (Fig. 2a), i.e., the temperature dependence of the conductivity for the olefins apart from ethylene is described satisfactorily by (4), which is derived from the law of corresponding states.

Figure 2b shows the deviations in the recommended reference data [31] and fitted results [28] from those calculated from (4), which on the whole do not exceed 2-3%. There are somewhat larger deviations in the [31] data for propylene (up to 3.3-6%) at 500-573 K, as in that range the [31] data are 3.5-5% less than the [18, 21] measuremnts, which agree with one another within ±1.0-1.5%.

LITERATURE CITED

1. A. Eucken, Phys. Z., 14, No. 1, 324-332 (1913).
2. A. Eucken, Forschung, 11, 6-11 (1940).
3. H. Senftleben and H. Gladisch, Z. Phys., 125, No. 7-10, 653-656 (1949).
4. I. M. Lenoir and E. W. Commings, Chem. Eng. Progr., 47, No. 5, 223-231 (1951).
5. H. Senftleben, Z. Angew. Phys., 5, No. 1, 29-33 (1953).
6. F. G. Keyes, Trans. ASME, 76, No. 5, 809-820 (1954).
7. J. D. Lambert and K. J. Cotton, Proc. R. Soc., A231, No. 1135, 280-290 (1955).
8. A. N. Chaikin and A. M. Markevich, Zh. Fiz. Khim., 32, No. 1, 116-120 (1958).
9. H. Cheung, L. A. Bromley, and C. R. Wilke, AIChE J., 8, No. 2, 221-228 (1962).
10. H. Senftleben, Z. Angew. Phys., 17, No. 2, 86-87 (1964).
11. I. A. Neduzhii, V. A. Kravets, and A. Ya. Kolomiets, Thermophysical Parameters for Hydrocarbons and Their Mixtures [in Russian], Kiev (1967), pp. 34-50.

12. I. A. Neduzhii and A. Ya. Kolomiets, Thermophysical Parameters of Substances [in Russian], Kiev (1969), pp. 84-90.
13. A. A. Tarzimanov and V. S. Lozovoi, Papers from Kazan' Chemical Engineering Institute, Heat and Mass Transfer Series [in Russian], Kazan' (1970), Issue 45, pp. 241-143.
14. A. S. Tirak'yan, Processing Gases and Gas Condensates: Abstract Coll. Nos. 2 [in Russian], Moscow (1971), pp. 6-9.
15. I. F. Golubev, I. B. Shpagina, and Yu. V. Mamonov, Organic-Synthesis Product Chemistry and Technology [in Russian], Trudy GIAP, Issue 8, Moscow (1971), pp. 81-90.
16. A. A. Tarzimanov and V. A. Arslanov, Heat and Mass Transfer [in Russian], Vol. 7, Minsk (1972), pp. 81-90.
17. A. S. Tirak'yan, Measurements on the Thermal Conductivities of Light Hydrocarbons and Their Mixtures: Ph. D. Thesis [in Russian], Moscow (1975).
18. A. Ya. Kolomiets, Measurements on the Thermal Conductivities of Light Hydrocarbon Gases and Their Mixtures: Ph. D. Thesis [in Russian], Moscow (1974).
19. Ya. M. Naziev and A. A. Abasov, Izv. Vyssh. Uchebn. Zaved., Gaz, No. 1, 63-66 (1968).
20. Ya. M. Naziev and A. A. Abasov, Gas Thermophysical Parameters [in Russian], Moscow (1970), pp. 25-27.
21. V. A. Kazaryan and N. N. Ryabtsev, Processing Gases and Gas Condensates: Abstract Coll. No. 5, Moscow (1971), pp. 3-10.
22. C. Parkinson, P. Mukhopadhyay, and P. Gray, J. Chem. Soc. Faraday Trans., Part 1, 68, No. 6, 1077-1085 (1972).
23. O. Vilim, Coll. Czech. Chem. Commun., 25, No. 4, 993-999 (1960).
24. N. A. Nesterov, V. A. Kurbatov, A. F. Zolotukhina, et al., Inzh. Fiz. Zh., 55, No. 2, 250-255 (1988).
25. Ya. M. Naziev and A. A. Abasov, Izv. Vyssh. Uchebn. Zaved., Gaz, No. 1, 81-84 (1969).
26. R. A. Mustafaev, The Thermophysical Parameters of Hydrocarbons at High State Parameters [in Russian], Moscow (1980).
27. R. A. Mustafaev, Teplofiz. Vysok. Temp., 14, No. 5, 979-983 (1976).
28. R. A. Mustafaev, A. O. Mekhrabov, and D. M. Gabulov, Gas Thermophysical Parameters [in Russian], Moscow (1976), pp. 82-87.
29. D. M. Vashchenko et al., The Thermodynamic and Transport Parameters for Ethylene and Propylene [in Russian], Moscow (1971), pp. 104-115.
30. A. A. Tarzimanov, Measurements on the Thermal Conductivities of Gases over Wide Ranges in the State Parameters: Doctorate of Science Thesis [in Russian], Kazan' (1972).
31. N. B. Vargaftik, L. P. Filippov, A. A. Tarzimanov, and E. E. Totskii, The Thermal Conductivities of Liquids and Gases [in Russian], Moscow (1978).
32. I. L. Knunyants, Encyclopedic Chemical Dictionary [in Russian], Moscow (1983).