

THERMAL CONDUCTIVITIES OF HEX-1-ENE, HEPT-1-ENE, OCT-1-ENE,
AND DEC-1-ENE AT 302-374 K

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Measurements are reported on the temperature dependence of the thermal conductivity for olefins in the vapor state.

One needs reliable data on the thermal conductivity λ for technically important substances such as olefins for calculations in designing equipment for petroleum refining, petrochemicals, the gas industry, and heavy organic chemicals.

Table 1 gives information on measurements on C_7H_{14} - $C_{10}H_{20}$ in the vapor state at $P \leq 1.01 \cdot 10^5$ Pa; there are no measurements for dec-1-ene below 469 K, while the [1] data for λ for hex-1-ene and hept-1-ene below 373 K and for oct-1-ene below 413 K are single values. Our analysis shows (Fig. 1) that the [1-3] results on λ for hept-1-ene in the overlapping temperature ranges are consistent within the overall errors ($\pm 3.4\%$) in the independent measurements, while the λ data of [1] for oct-1-ene represent overestimates (by up to 3.9%) relative to [3, 4]. The [1] measurements for propylene are low relative to the [5, 6] results, which are consistent one with the other within ± 0.1 -1.5%; the discrepancy attains 6.5%, which exceeds the overall error in the independent measurements and processing (± 2.4 -3.4%).

These features have made it necessary to measure the vapor conductivities for hex-1-ene, hept-1-ene, oct-1-ene, and dec-1-ene at 302-374 K; we used dec-1-ene containing not less than 99.9% of the main substance, while the purities for the other substances were not less than 99.99%.

We used an absolute stationary form of the heated-wire method; see [7] for the theory, the cell design, and the measurement methods. A difference from [7] was that we used a cell having the following geometry: internal diameter (molybdenum glass tube type 3S5K) 3.649×10^{-3} m, outside diameter 5.542×10^{-3} m, diameter of platinum wire in internal resistance thermometer acting also as heat source 0.082×10^{-3} m, measurement section length 103.159×10^{-3} m, potential-lead diameter 0.071×10^{-3} m, layer thickness 1.783×10^{-3} m, eccentricity between wire axis and tube axis 0.01×10^{-3} m; platinum resistance thermometer characteristics: resistance of internal thermometer at 273.15 K 2.07391Ω , temperature coefficient of resistance for internal thermometer $3.9850 \times 10^{-3} K^{-1}$, resistance of outside thermometer at 273.15 K 14.38852Ω , and temperature coefficient of resistance for outer thermometer $3.8908 \times 10^{-3} K^{-1}$. Figure 2 shows the apparatus. The part of the apparatus between the vacuum pump and the working chamber 3, which includes the stopcocks 13-18, was made of 1Kh18N10T stainless steel. Co-var tubes joined the glass parts to the metal ones.

The liquids were contained in the glass vessels 11 and the air was removed by means of the vacuum pump; the entire system above the stopcocks 15 was evacuated to a residual pressure of 5×10^{-3} mm Hg. With stopcock 14 closed, working chamber 3 was filled with the vapor, whose pressure was measured by the mercury manometer 7. Then the thermostat heaters were switched on and a set temperature was attained; after a uniform temperature distribution had been attained in the cell, the measurements were made.

The thermal conductivity is defined by

$$\lambda = A \frac{Q_T}{\Delta T}, \quad (1)$$

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TABLE 1. Measurements on Olefin Vapor Thermal Conductivity

Authors	Year	Main component, %	Temp., K	Method	Error
<u>Hex-1-ene</u>					
Naziev and Abasov [1]	1968	99.9	293-633	Regular mode	±1.4
<u>Hept-1-ene</u>					
Naziev and Abasov [1]	1968	99.5	293-633	Ditto	±1.4
Naziev and Abasov [2]	1969	99.5	373-623	Ditto	±1.4
Mustafaev [3]	1980	99.8	383-678	Monotone heating	±2
<u>Oct-1-ene</u>					
Naziev and Abasov [1]	1968	99.6	293-633	Regular mode	±1.4
Mustafaev [4]	1976	99.0	413-678	Monotone heating	±2
Mustafaev [3]	1980	99.8	418-678	Ditto	±2
<u>Dec-1-ene</u>					
Mustafaev [4]	1976	99.0	473-673	Monotone heating	±2
Mustafaev [3]	1980	99.8	469-654	Ditto	±2

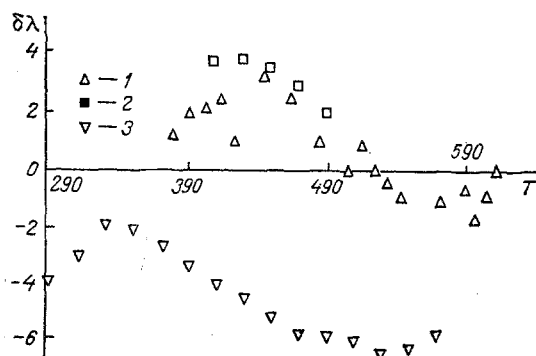


Fig. 1. Deviations between the measured olefin conductivities [1] and published data: 1) hept-1-ene from [4] values; 2) oct-1-ene [4, 5]; 3) propylene [6, 7]; $\delta\lambda$, %; T, K.

where $A = \ln d_2/d_1 / (2\pi l)$, with d_1 the wire diameter for the internal resistance thermometer, d_2 the internal diameter in the glass tube, and l the measurement length; Q_T is the amount of heat transmitted by conduction through the layer in the measurement section in W; and ΔT is the temperature difference across the layer of vapor between the filament and the internal wall in K.

The corrections appropriate to the method [7] were applied in calculating the thermal conductivity from (1).

The apparatus was tested with 99.993% argon; the results agreed with reference data [8] within ±1%.

Table 2 gives the measurements. The errors have been calculated by estimating the random error and the residual systematic error, whose distributions were correspondingly as in a t distribution and uniform, as recommended in [9] for thermophysical measurements. In all cases, we used 0.95 confidence probability.

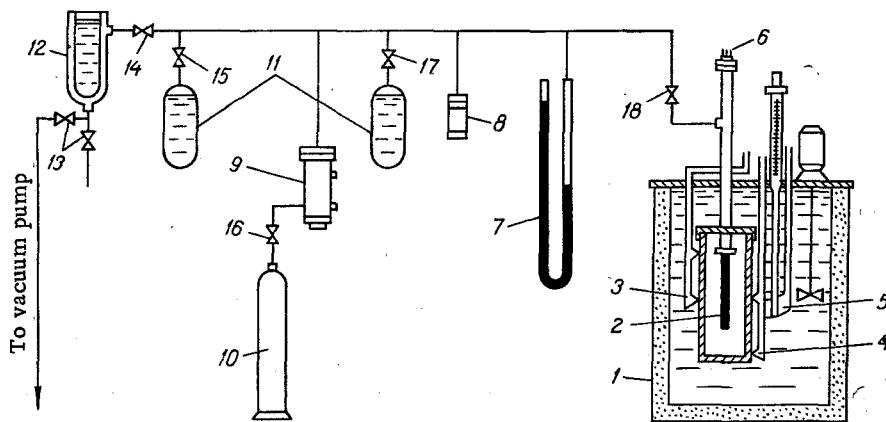


Fig. 2. Apparatus for determining thermal conductivity of organic vapors: 1) thermostat; 2) measurement cell; 3) working chamber; 4) temperature monitoring system; 5) temperature control system; 6) electrovacuum socket; 7) MBP mercury manometer; 8) LT-2 pressure gauge; 9) gas drying system; 10) cylinder containing calibration gas; 11) glass vessels containing liquid olefins; 12) nitrogen trap; 13-18) vacuum valves.

TABLE 2. Measured Thermal Conductivities for Olefin Vapors
 $\lambda \times 10^3$ W/m \cdot K

P, Pa	T, K	λ	P, Pa	T, K	λ
122,95 \cdot 10 ²	Hex-1-ene		9,87 \cdot 10 ²	352,21	16,03
	305,10	12,99		360,21	16,74
	308,94	13,23		363,59	17,28
	314,02	13,75		368,20	17,79
	320,90	14,44		368,76	17,86
	329,10	15,14		Oct-1-ene	
	337,19	15,96		303,68	10,72
	346,07	16,77		307,51	10,88
	347,44	17,01		307,54	10,96
	353,25	17,64		308,27	11,06
	356,99	18,10		317,85	11,75
	365,18	19,04		322,18	12,07
	370,58	19,58		325,93	12,41
	23,85 \cdot 10 ²	Hept-1-ene		328,37	12,45
301,67		11,62	329,02	12,59	
310,34		12,26	339,48	13,45	
320,34		13,03	349,32	14,31	
328,00		13,66	360,20	15,38	
337,03		14,48	369,50	16,22	
347,28		15,36	Dec-1-ene		
355,58		16,21	304,65	9,14	
374,33		18,33	305,83	9,12	
46,75 \cdot 10 ²		306,05	11,92	307,80	9,18
		309,04	12,14	314,15	9,60
		313,94	12,53	319,41	9,89
		315,91	12,65	327,65	10,51
		321,53	13,15	333,93	10,96
	325,32	13,37	344,82	11,71	
	330,48	14,02	353,91	12,31	
	332,81	14,16	358,23	12,88	
	343,00	15,09	367,92	13,48	
	346,61	15,27			

From (1), the limiting possible relative systematic error is [10]

$$\delta\lambda_{\text{sys.}} = 1,1 \sqrt{\left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta Q_T}{Q_T}\right)^2 + \left[\frac{\Delta(\Delta T)}{\Delta T}\right]^2}, \quad (2)$$

where Δ denotes the absolute error in measuring the quantity.

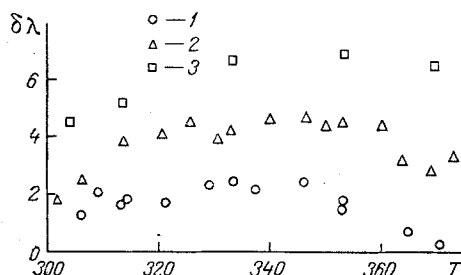


Fig. 3. Deviations in the measured olefin conductivities [1] from our data: 1) hex-1-ene; 2) hept-1-ene; 3) oct-1-ene.

The limiting random relative error for λ is [10, 11]

$$\delta\lambda_{\text{ran}} = 2.23 \frac{\sqrt{\sum_{i=1}^n \frac{(\lambda_i - \bar{\lambda})^2}{n(n-1)}}}{\bar{\lambda}},$$

where $n = 10$ is the sample volume, λ_i the measured value, and $\bar{\lambda} = \frac{1}{n} \sum_{i=1}^n \lambda_i$ the arithmetic mean.

This did not exceed 0.44%.

Direct and indirect measurements on the quantities in (1) gave $\Delta A/A = 0.35\%$, $\Delta Q_T/Q_T = 0.41\%$, and $\Delta(\Delta T)/\Delta T = 0.99\%$; the maximum possible relative systematic error in a single measurement from (2) is 1.2%.

The overall limiting relative error in λ is [11]

$$\delta\lambda_{\Sigma} = \sqrt{\delta\lambda_{\text{sys}}^2 + \delta\lambda_{\text{ran}}^2}$$

and is 1.3%.

The [1] measurements are compared with ours in Fig. 3; the agreement for hex-1-ene is satisfactory, while the [1] λ for hept-1-ene and oct-1-ene are systematically too high, correspondingly by 4.7 and 6.9%. In [1, 2], no description is given of the procedure for filling the working gap in the autoclave with the substances in the gas or vapor states, and it is not stated whether the air was first removed and how. Air in the working gap could distort the conductivities. We consider that this may be a reason why the [1] data deviate from the [3-6] ones and from ours.

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