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# RADIATIVE—CONDUCTIVE HEAT TRANSFER IN LIQUID ORGANIC COMPOUNDS AT 373-473°K

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Experimental and numerical-solution results are presented for radiative—conductive heat transfer (RCHT) in planar layers of organic liquids at elevated temperatures.

Radiative—conductive heat transfer is of interest in relation to working media with weak absorption in the near infrared (IR), particularly in improving methods of calculating equipment for wide temperature and pressure ranges. If one neglects radiation, large errors occur, particularly at elevated temperatures, since the main transport parameter is the effective thermal conductivity $\lambda_{ef}$, which has a conductive component $\lambda_c$ and a radiative one $\lambda_r$.

The problem can be considered in the gray approximation if the effect of radiation is small (up to 10%), or it can be treated numerically from a selective model if there is a considerable radiation effect. Experiment is required to evaluate the assumptions made in the model.

Most experiments deal with RCHT for solids and molten materials [1]; effective thermal conductivities have been determined for organic liquids only at atmospheric pressure and temperatures up to 373°K [2-7].

An apparatus has been devised [8] for recording the temperature and heat-flux distributions by interferometry on planar layers of organic compounds at 293-473°K and pressures up to 1 MPa. The method is fast and sensitive and allows one to visualize the processes. One can judge the radiative component from the nonlinearity in the temperature distribution and can derive it from the $\lambda_{ef}/\lambda_c$ ratios deduced by two methods: from the relative plane-layer method [2] and from the method due to Girgull and Schodel [4] as modified for high temperatures. The heaters and the opaque boundaries are provided by silica plates with films of invar and platinum evaporated onto the surfaces. The integral degree of blackness normal to the surface has been measured at 293°K with a TRM I thermoradiometer, whose spectral sensitivity covers the range 4-40 μm, the values for the upper and lower plates being $\varepsilon_s = 0.15$ and $\varepsilon_s = 0.16$ correspondingly. High-temperature experiments required a three-stage system, which included air and liquid thermostats, as well as an electronic system for regulating the temperature difference across the layer of liquid ($\Delta T = 0.5$–$2$ K). The maximal relative errors in the measured $\lambda_{ef}/\lambda_c$ have been calculated by means of error theory in accordance with the standardization documents [9-12] and did not exceed ±2%.

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TABLE 1. Calculated Coefficients in Empirical $\lambda_{ef}/\lambda_c = A(T - 273)^2 + B(T - 273) + C$ Formulas, $\Delta T = 1$ K

| Compound | $h$, mm | Coefficients | | |
|---|---|---|---|---|
| | | $A \cdot 10^6$ | $B \cdot 10^3$ | $C$ |
| n-Heptane | 5,28 | 3,00 | 1,32 | 1,114 |
| n-Nonane | 5,28 | 2,92 | 1,04 | 1,113 |
| n-Decane | 5,28 | 2,18 | 1,02 | 1,094 |
| | 3,32 | —2,20 | 2,10 | 0,991 |
| | 1,67 | —0,80 | 1,38 | 0,968 |
| n-Dodecane | 5,28 | 3,24 | 0,75 | 1,083 |
| | 3,32 | 6,00 | 3,04 | 0,914 |
| | 1,67 | 0,02 | 1,14 | 1,001 |
| n-Tridecane | 5,28 | 1,87 | 1,11 | 1,053 |
| | 3,32 | 1,33 | 0,76 | 1,056 |
| | 1,67 | 1,39 | 0,67 | 1,002 |
| n-Pentadecane | 5,28 | 2,14 | 1,03 | 1,044 |

TABLE 2. Calculated Coefficients in Empirical $\lambda_{ef}/\lambda_c$ $bn_C + c$ Formulas

| Temp., °K | Coefficients | | |
|---|---|---|---|
| | $a \cdot 10^3$ | $b \cdot 10^2$ | $c$ |
| 373 | 1,583 | —4,938 | 1,5541 |
| 393 | 1,845 | —5,700 | 1,6352 |
| 413 | 1,726 | —5,416 | 1,6573 |
| 433 | 1,904 | —5,833 | 1,7161 |
| 453 | 2,080 | —6,547 | 1,8119 |
| 473 | 2,381 | —7,536 | 1,9250 |

TABLE 3. Values of $\lambda_{ef}/\lambda_c$ for Saturated Hydrocarbons, $\Delta T = 1$°K

| Substance | Formula | $h$, mm | Temperature, °C | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 373 | 393 | 413 | 433 | 453 | 473 |
| n-Decane | $C_{10}H_{22}$ | 1,67 | 1,10 | 1,13 | 1,15 | 1,17 | 1,19 | 1,21 |
| | | 3,32 | 1,19 | 1,21 | 1,24 | 1,27 | 1,30 | 1,32 |
| | | 5,28 | 1,22 | 1,24 | 1,28 | 1,32 | 1,35 | 1,39 |
| n-Dodecane | $C_{12}H_{26}$ | 1,67 | 1,08 | 1,10 | 1,13 | 1,14 | 1,16 | 1,19 |
| | | 3,32 | 1,16 | 1,17 | 1,21 | 1,23 | 1,24 | 1,28 |
| | | 5,28 | 1,18 | 1,22 | 1,26 | 1,29 | 1,32 | 1,36 |
| n-Tridecane | $C_{13}H_{28}$ | 1,67 | 1,07 | 1,09 | 1,11 | 1,13 | 1,15 | 1,18 |
| | | 3,32 | 1,14 | 1,17 | 1,18 | 1,21 | 1,24 | 1,26 |
| | | 5,28 | 1,18 | 1,21 | 1,25 | 1,28 | 1,31 | 1,35 |

We used saturated hydrocarbons as widely employed in organic synthesis and oil refining. The liquids were dried and distilled, and the purity was checked by measuring the boiling point, refractive index, and IR absorption spectrum. The deviations in the refractive indices from the data of [13] did not exceed $2 \times 10^{-4}$.

Under these conditions, a rise in temperature causes on the one hand an increase in the energy emitted by the boundary surfaces and the liquid itself and on the other a reduction in the absorption in the liquid. This results in increased nonlinearity in the temperature pattern and increase in $\lambda_{ef}/\lambda_c$ with temperature and layer thickness, with $\lambda_{ef}/\lambda_c = f(T)$ varying more for large thicknesses. For example, with thickness h = 5.28 mm and T = 473°K, $\lambda_{ef}/\lambda_c$ took the values 1.33 for pentadecane, 1.38 for n-decane, and 1.51 for n-heptane.

Regression analysis was applied to the $\lambda_{ef}/\lambda_c$ as functions of temperature and number of carbon atoms $n_C$ in the molecule. Tables 1 and 2 give the coefficients in the regression equations.

We found that the radiative component of the total heat flux in the n-alkane series varied considerably between $n_C = 7$ and $n_C = 10$, but with little variation above that range, which was characteristic of all temperatures and thicknesses.

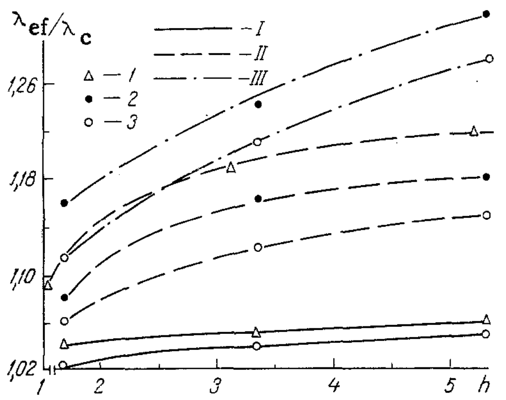

Fig. 1

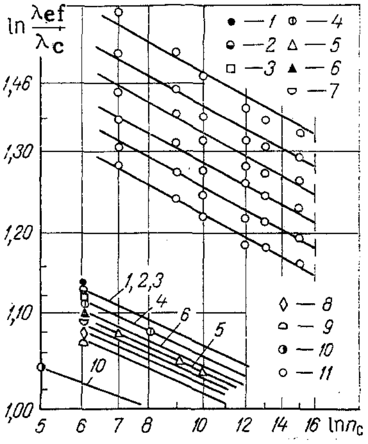

Fig. 2

Fig. 1. Dependence of $\lambda_{ef}/\lambda_c$ on layer thickness for n-dodecane: 1 and 2) measurements [6] and our results correspondingly; 3) calculations from selective model [16]; I) 293 K; II) 373; III) 473.

Fig. 2. Dependence of $\lambda_{ef}/\lambda_c$ on number of carbon atoms in the molecole: 1) saturated hydrocarbons (smoothed data of [6]); 2) unsaturated hydrocarbons; 3) cycloparaffins; 4) ethers; 5) ketones; 6) halogenated derivatives; 7) aldehydes; 8) amines; 9) esters; 10) carboxylic acids (data of [3]); 11) saturated hydrocarbons in the range from 373°K (lower line) to 473°K (upper line) at intervals of 20°K (our results); $\varepsilon_1 = 0.15$; $\varepsilon_2 = 0.16$; h = 5.28 mm.

Table 3 gives $\lambda_{ef}/\lambda_c$ for various thicknesses, where the values reflect the radiative component and approach a limit. The increase in $\lambda_{ef}/\lambda_c$ is the more pronounced the higher the temperature (Fig. 1).

These measurements allowed us to check the model devised at the All-Union Electrothermal Equipment Research Institute under the direction of N. V. Marchenko, which is based on solving the stationary problem for a planar layer of selective nonscattering semitransparent medium having diffusely reflecting boundaries [4]. The selective model was used for the saturated hydrocarbons because of their IR spectra, which have pronounced selectivity in the wave number range coincident with the peak in the thermal radiation spectrum. The IR spectra were approximated as segments of straight lines and parabolas, with summation in accordance with Gauss quadrature formulas. An initial linear temperature distribution was assumed in the calculations, which was determined from the boundary values.

Numerical methods gave a nonlinear antisymmetric temperature distribution with a point of inflection at the middle of the layer, which reproduced the observed pattern; there were slight deviations (within the experimental error) for the radiative component when radiation contributed up to 30%, which shows that the assumptions in the model are correct.

The theoretical and observed $\lambda_{ef}/\lambda_c$ curves as functions of layer thickness were identical in form (Fig. 1).

There are major difficulties in measuring $\lambda_{ef}/\lambda_c$ at elevated temperatures, and much initial information is required in the numerical calculations, so we used a method enabling one to determine the radiation contributions approximately for homologous series and derivatives of saturated hydrocarbons (unsaturated hydrocarbons, cycloparaffins, halogen derivatives, aldehydes, amines, esters, and carboxylic acids). We recorded the IR absorption spectra with a Specord IR spectrophotometer over the range 2-25 μm at 293-473°K. The temperature dependence for the IR spectra of the saturated hydrocarbons showed that the integral absorption has a negative temperature coefficient, which is due to the behavior of the molecular interaction, although the distribution of the molecules over the energy states is almost unaltered [15].

The intermolecular force potential varies smoothly with temperature, and therefore so do the spectroscopic parameters, with the integral absorption decreasing and therefore $\lambda_{ef}/\lambda_c$ increasing. The Planck function is displaced to short wavelengths, where the liquids are most transparent, which accentuates the increase in $\lambda_{ef}/\lambda_c$.

The values of $\lambda_{ef}/\lambda_c$ for saturated hydrocarbon derivatives at 293°K [3] and for these hydrocarbons themselves at 373-473°K can be used with the temperature dependence of the IR spectra to predict that the relations between the $\lambda_{ef}/\lambda_c$ for the different homologous series at 293°K shown in Fig. 2 will persist at elevated temperatures. The basic reference straight lines were provided by ones constructed from the measured $\lambda_{ef}/\lambda_c$ for the saturated hydrocarbons in the above temperature range.

## NOTATION

$\lambda_{ef}$, $\lambda_c$, $\lambda_r$, effective, conductive, and radiative thermal conductivities respectively, W/(m·K); $n_C$, number of carbon atoms in chain; T, absolute temperature, K; h, thickness of liquid layer, mm; $\varepsilon_s$, integral emissivity normal to the surface.

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