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INVESTIGATION OF THERMAL CONDUCTIVITY OF LIQUID FORMATES AT HIGH TEMPERATURES AND PRESSURES

R. A. Mustafaev and T. P. Musaev

UDC 536.6

Experimental data on the thermal conductivity of butyl formate and octyl formate in a wide range of temperatures and pressures are given.

The experimental investigation of the thermal conductivity of liquids at high temperatures and pressures involves considerable technical difficulties. The conduction of investigations at high pressures and high temperatures necessitates the design of special and complex apparatus.

The data in [1] mainly characterize the temperature dependence of the thermal conductivity of formates at atmospheric pressure. It is only in recent time that investigations of the thermal conductivity of formates in relation to temperature and pressure have been undertaken. In [2], e.g., the results of measurement of the thermal conductivity of formates in relation to temperature at relatively low pressures (1-49 MPa) are given.

In the present paper, which represents the continuation of previous research [3-9], we give the results of an experimental investigation of the thermal conductivity of butyl and octyl formates at temperatures from room to 620°K and pressures up to 147 MPa. The measurements were made by the steady heating method on a newly designed version of a cylindrical bicalorimeter.

The theory of the method and the measurement procedure are described in detail in [6, 9].

The bicalorimeter consists of two coaxial cylinders. The gap between the cylinders is filled with the liquid under investigation. The inner cylinder (core) is made of M1 copper. The working surfaces of the core are thoroughly ground, chrome-plated, and polished. The outer cylinder is a massive copper block, into which a tube of 1Kh18N9T stainless steel is pressed. As distinct from the previous design [6], lens sealing was used to maintain the high pressure.

The main dimensions of the bicalorimeter are: inner diameter of copper block 9.99 ± 0.01 mm, diameter of copper core 9.010 ± 0.002 mm, length of measuring section 80 mm.

The experimental determination of thermal conductivity reduces to measurement of the time lag of the core temperature relative to the block temperature. For these measurements we used an R-345 potentiometer and a 51-SD timer, and for creation and measurement of the pressure we used an MP-2500 loaded-piston gauge and a set of standard gauges. In the calculation of the thermal conductivity we introduced all the corrections

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Ch. Il'drym Azerbaidzhan Polytechnic Institute, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 37, No. 2, pp. 324-328, August, 1979. Original article submitted November 22, 1978.

TABLE 1. Experimental Values of Thermal Conductivity of Liquid Formates ($\lambda \cdot 10^{-4}$ W/m·degK) in Relation to Temperature and Pressure

T, °K	P, MPa							
	0,098	19,6	39,2	58,8	78,4	98,0	117,6	147,0
				Butyl formate				
300	1357	1465	1569	1648	1750	1839	1924	2025
312	1324	1434	1535	1689	1749	1834	1924	2019
324	1309	1400	1500	1599	1705	1778	1900	1999
336	1250	1400	1495	1599	1688	—	1874	1975
361	1204	1319	1439	1538	1650	1745	1834	1943
379	1144	1280	1395	1504	1614	1684	1803	1927
391	—	1290	1374	1508	1598	—	1781	1924
397	—	1234	1398	1474	1575	1675	1780	1900
409	—	1232	1338	1474	1550	1670	1755	1875
421	—	1209	1339	1428	1534	1645	1749	1858
427	—	1174	—	1409	1514	1609	1731	1804
445	—	1124	1254	1378	1498	1589	1704	1844
481	—	1055	1200	1324	1426	1534	1635	—
487	—	1074	1176	1323	1403	1544	1650	1799
500	—	1034	1150	1297	1398	1500	1650	1778
512	—	1000	1145	1260	1374	1484	1619	1745
518	—	0976	1125	1245	1370	1475	1610	1754
524	—	990	1109	1227	1350	1470	1600	1724
549	—	934	1074	1185	1320	1425	1564	1699
574	—	900	1045	1150	1314	1400	1534	1682
580	—	904	1017	1134	1283	1405	1541	1685
592	—	874	999	1134	1255	1404	1507	1674
600	—	900	1001	1154	1270	1399	1524	1655
618	—	850	1009	1110	1230	1384	1510	1645
				Octyl formate				
306	1347	1438	1522	1599	1677	1725	1812	1885
324	1317	1406	1487	1575	1635	1712	1775	1890
336	1281	1395	1475	1545	1626	1695	1769	1876
366	1215	1342	1432	1502	1555	1654	—	1840
373	1217	1310	1400	1480	1565	1648	1725	1823
385	1186	1294	—	1465	1552	1630	1695	—
397	—	1275	1345	1450	1525	1610	1695	1800
415	—	1240	1315	1420	1513	1580	1672	1786
421	—	1225	1325	1406	1482	1588	1675	1719
433	—	1192	1288	1385	1490	1575	1665	1765
439	—	1188	1286	1365	1455	1556	1647	1755
451	—	1176	1250	1348	1445	1540	1638	1745
463	—	1132	1245	1325	1435	1520	1604	1747
481	—	1115	1210	1295	1390	1495	1584	1718
493	—	1085	1180	1295	1375	1486	1573	1687
512	—	1040	1155	1265	1320	1448	1562	1697
518	—	1020	1135	1245	1345	1446	1547	1682
531	—	—	1135	1220	1325	1415	1534	1667
543	—	1015	1115	1215	1338	1420	1540	1652
555	—	975	1100	1215	1306	1385	1497	1638
562	—	980	1075	1170	1285	1395	1498	1632
580	—	950	1065	1165	—	1365	1467	1624
592	—	945	1045	1140	1255	1350	1464	1609
600	—	925	1030	1155	1262	1362	1423	1599
612	—	920	1025	1130	1245	1345	1454	1599
618	—	900	1020	1125	1236	1390	1447	1595

appropriate to this method [9]. No radiation correction was introduced, since we had no data on the absorption spectra of the investigated substances. The calculated maximum error of the measurement was 2%. The reproducibility of the experimental data obtained with the same state parameters was within 1%. The possible effect of convection was checked by conducting a series of experiments at different core heating rates (temperature differences). The good convergences of the results of measurement indicated that convection had no effect on the results of measurement.

The obtained experimental results are given in Table 1 and were used to construct isobars. For their internal matching we also plotted isotherms by corresponding sections. Figure 1 shows the thermal conductivity isobars and isotherms for octyl formate. The thermal conductivity isobars and isotherms for butyl formate were similar.

As Fig. 1 shows, the isobars and isotherms are curved lines and are arranged in a definite sequence without intersecting one another. The effect of pressure on the thermal conductivity decreases at high pressures. The temperature coefficient of the thermal conductivity decreases with increase in pressure.

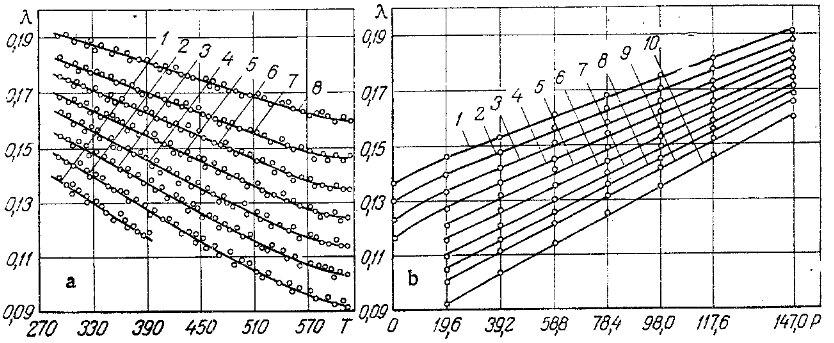

Fig. 1. Isobars (a) and isotherms (b) of thermal conductivity of octyl formate: a: 1) 0.098; 2) 19.6; 3) 39.2; 4) 58.8; 5) 78.4; 6) 98.0; 7) 117.6; 8) 147.0 MPa. b: 1) 300; 2) 330; 3) 360; 4) 390; 5) 420; 6) 450; 7) 480; 8) 510; 9) 540; 10) 600°K. λ, W/m·degK; T, °K; P, MPa.

It is of interest to compare the results that we obtained with those available in the literature. A comparison with the data of [1] at atmospheric pressure shows that for butyl formate they are 2-3.8% higher than ours, and for octyl formate 2-3.4% higher. A comparison of the results of [2] at 39.2 MPa with ours shows that the data of [2] are 1-2.8% higher than ours.

To determine the effect of pressure on the thermal conductivity of the liquids we used the Missenard formula [10]. However, as investigations showed, it represented the experimental data with an error of 5%, which increased with increase in temperature.

Description of the thermal conductivity in terms of the parameters measured directly in the experiments, i.e., in terms of the pressure and temperature, is the best approach. Hence, in recent time wide use has been made of the method proposed by Rivkin [11] for description of the thermal conductivity of ordinary and heavy water. According to this method the lines of constant thermal conductivity in P – T coordinates are straight lines.

An analysis of our experimental data shows that the lines $\lambda = \text{const}$ for the investigated formates are not straight, but curved, especially in the region of high temperatures.

An analysis of the obtained thermal conductivity data for formates shows that the isobars in coordinates $\lambda n_C^{1/5} = F(\tau)$ are straight lines, i.e., for each isobar for the same reduced temperatures $\tau = T/T_b$ the condition $\lambda n_C^{1/5} = \text{const}$ is fulfilled.

The last condition enabled us to obtain the general equation

$$\lambda = \frac{1}{n_C^{1/5}}\left[(0.285 + 3.52\cdot 10^{-5}P) - (0.1165 - 3\cdot 10^{-5}P)\tau\right]$$

for the calculation of thermal conductivity in a wide range of temperatures and pressures.

Figure 2 compares the obtained experimental data with the values calculated from this equation in a wide range of pressures at 420 and 570°K. As Fig. 2 shows, the proposed equation represents fairly accurately the relation $\lambda = F(P, T)$, and the mean deviation of the calculated thermal conductivity values from the experimental values is 2-3%.

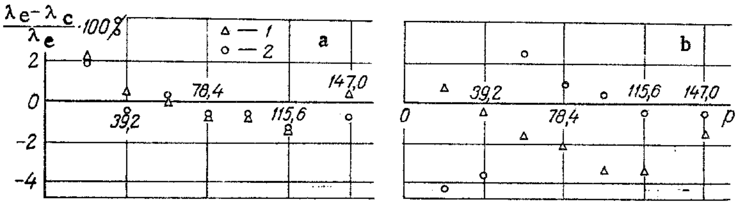

Fig. 2. Comparison of experimental thermal conductivity data for butyl formate (1) and octyl formate (2) with calculated values at: a) 420; b) 570°K.

NOTATION

T_b, normal boiling point of liquid at atmospheric pressure; n_C, number of carbon atoms in molecule.

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CONDUCTIVITY IN ALLOTROPIC PHASE TRANSITIONS

G. N. Dul'nev, I. K. Meshkovskii,
V. V. Novikov, and I. A. Sokolov

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A method is given for calculating the resistivity as a function of temperature in the presence of structural phase transitions in solids.

Many studies have been performed [1-3] on the conductivity in the presence of allotropic phase transitions, which is a subject related to the design of critical resistors. However, the basic characteristic, viz., the electrical resistance R as a function of temperature T, has so far been described only by approximation.

Here we present a quantitative theory that employs the initial and final critical conductivities with the heat of phase transition and the temperature range of the transition to calculate the resistance as a function of temperature. Realistic objects are characteristic critical thermistors with structural phase transitions of different kinds: the metal – semiconductor transition in VO_2 [4-8] and the ferroelectric – paraelectric transition in $BaTiO_3$ ceramic [1].

The initial model concepts include the existence of a structurally homogeneous phase below the transition point, which is characterized by a specific conductivity σ_1 and a temperature coefficient of the conductivity α_1.

As the temperature rises, deviations from σ_1 as corrected by α_1 begin to appear at $T = T_i$; in the range from T_i to T_f there is a change in the electrical conductivity, and above T_f there is a structurally homogeneous phase with conductivity σ_2 and temperature coefficient of conductivity α_2.

There is a phase transition in the range T_i–T_f which is due to the difference in chemical potential between the two phases. The new phase arises in the old matrix in the theory of heterogeneous transitions [9], which occurs by nucleation and growth of the new phase. We assume that the major changes in concentration are due to the growth, which occurs at the nuclei. In turn, nucleation is due to heterophase fluctuations. The nucleation probability is related to the particle mobility via the factor $\exp(-U/KT)$, in which U is an activation energy [9]. The overall concentration of such nuclei is proportional to the internal energy of the solid, so the temperature dependence of the concentration tends to run parallel to the temperature dependence of the specific heat.

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