ON THE FLUID THERMAL ACTIVITY COEFFICIENT USING WATER AS AN EXAMPLE

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In conformity with the experimental results on the density, heat conductivity, specific heat, and viscosity of water, it is established that 1) the fluid thermal activity coefficient can be expressed in a form analogous to the equation of state, and 2) a linear dependence exists between the fluid thermal activity and heat conductivity coefficients as well as the viscosity.

The concept of the thermal activity of a substance, introduced by A. V. Lykov [1], is expressed by the quantity

$$\varkappa = \sqrt{\rho \lambda c_p}\,. \tag{1}$$

Since $\varkappa$ is defined in terms of the mentioned parameters, which are functions of the temperature and pressure, then the thermal activity coefficient should evidently be considered a thermophysical parameter dependent also on the temperature and pressure, i.e., $\varkappa = f(T, p)$.

An original method of measuring the fluid thermal activity coefficient to accuracy on the order of ~3% is proposed in [2-4], which is not associated with the use of the quantities ρ, λ and c_p which are difficult to determine.

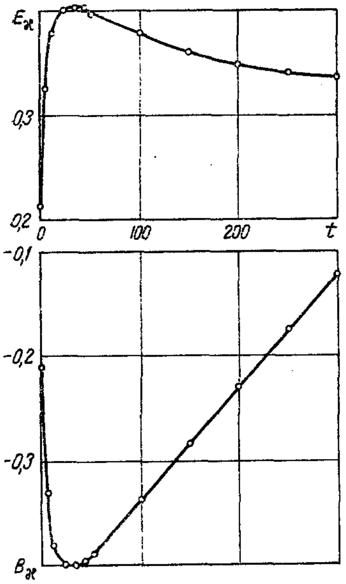

Fig. 1

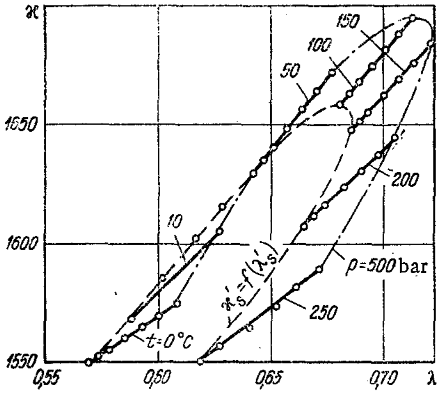

Fig. 2

Fig. 1. Values of the coefficient $E_\varkappa (cm^3/g)^4$, $B_\varkappa (cm^3/g)$ evaluated by means of (3).

Fig. 2. Dependence of the thermal activity coefficient $\varkappa (J/m^2 \cdot deg \cdot sec^{1/2})$ on λ (W/m · deg).

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TABLE 1. Comparison between the Values of the Thermal Activity Coefficient of Water $\varkappa$ (J/m^2 · deg · sec$^{1/2}$), Calculated by Means of (1) (first row) and (3) (second row)

bar	$\varkappa$ at the temperature, °C										
	0	10	20	30	40	50	100	150	200	250	300
p_s	1548,9 1548,9	1567,2 1567,2	1585,3 1585,3	1602,2 1601,7	1616,2 1616,2	1629,8 1629,8	1657,5 1657,5	1646,5 1646,5	1606,8 1606,8	1549,5 1549,5	1489,9 1489,9
10	1549,7 1549,4	1569,1 1568,1	1569,1 1568,1	1604,2 1602,6	1618,1 1617,1	1631,0 1630,5	1658,7 1658,1	1647,6 1646,8	— —	— —	— —
50	1551,5 1551,5	1572,1 1571,6	1591,9 1589,5	1607,9 1606,0	1623,1 1620,4	1634,5 1633,8	1662,2 1661,4	1650,7 1649,8	1610,4 1609,6	1550,1 1550,4	— —
100	1554,0 1553,9	1576,0 1575,8	1596,2 1593,9	1613,6 1610,3	1627,3 1624,6	1638,9 1637,9	1666,8 1665,2	1653,9 1653,6	1613,7 1613,5	1553,9 1555,0	1491,2 1491,7
150	1556,7 1556,4	1581,6 1580,1	1600,3 1598,2	1618,1 1614,5	1632,6 1628,9	1643,8 1642,0	1670,2 1669,2	1657,3 1657,6	1617,4 1617,4	1558,2 1559,5	1493,7 1497,4
200	1559,4 1558,9	1584,6 1584,3	1604,7 1602,5	1621,1 1618,8	1636,8 1633,0	1648,4 1646,3	1673,9 1673,3	1661,7 1661,4	1622,2 1621,9	1563,4 1563,9	1495,9 1503,2
250	1562,5 1561,4	1589,3 1588,6	1607,8 1606,8	1625,5 1623,2	1640,7 1637,2	1651,9 1650,4	1678,6 1677,1	1664,9 1665,3	1625,9 1625,6	1568,8 1568,2	1500,0 1508,3
300	1564,1 1564,0	1592,8 1592,8	1612,1 1611,1	1629,5 1627,3	1643,6 1641,5	1656,5 1654,4	1682,1 1681,1	1668,4 1669,1	1629,8 1629,7	1572,3 1572,4	1504,6 1513,5
350	1567,1 1566,4	1596,1 1597,1	1615,3 1615,4	1633,5 1631,6	1648,6 1645,5	1659,9 1658,3	1685,7 1684,8	1672,8 1672,9	1633,7 1633,5	1577,2 1576,6	1509,4 1518,2
400	1569,0 1568,9	1599,2 1601,2	1619,7 1619,7	1636,3 1635,8	1652,3 1649,6	1663,6 1662,6	1689,3 1687,7	1676,1 1676,5	1637,7 1637,3	1581,2 1580,7	1513,5 1522,2
500	1574,1 1574,0	1605,8 1609,6	1626,3 1628,3	1642,8 1644,2	1657,3 1657,9	1670,6 1670,6	1696,4 1696,4	1684,1 1683,9	1644,8 1644,9	1588,7 1588,6	1520,6 1531,4

The author proposes a method of determining the fluid thermal activity coefficient for high state parameters; it is hence sufficient to have the values of ρ, λ and c_p in just two points at a given temperature.

A check has shown that the fluid thermal activity coefficient can be expressed in a form analogous to the equation of state. Taking into account that the equation of state [5]

$$\frac{pv}{RT} = 1 + B\rho + E\rho^4 \tag{2}$$

describes the specific volume of water in the 0-350°C temperature range and for pressures from p_s to 1000 bar within the tolerances established by the 1964 skeleton tables of water and steam [6], the thermal activity coefficient of water can be expressed as:

$$\frac{\varkappa}{\varkappa_s'} = 1 + B_\varkappa\rho + E_\varkappa\rho^4. \tag{3}$$

The values of $\varkappa$ calculated by means of (1) are presented in Table 1. The needed values of the quantities ρ, λ and c_p are taken from [6].

TABLE 2. Values of the Coefficients $B_\varkappa$ (cm^3/g) and $E_\varkappa$ (cm^3/g)^4 in (3) for Water as Calculated by Means of (6), (7) and (5)

t, °C	$-B_\varkappa$	$E_\varkappa$	t, °C	$-B_\varkappa$	$E_\varkappa$
0	0,21302	0,21315	100	0,33193	0,37716
10	0,37848	0,37894	150	0,27945	0,36249
20	0,39932	0,40148	200	0,22698	0,35109
30	0,39936	0,40465	250	0,17450	0,34180
40	0,39455	0,40397	300	0,12203	0,33744
50	0,38440	0,39849			

TABLE 3. Values of the Coefficients of (12) and (13) for Water

t, °C	By (12)		By (13)	
	$m_1(t)$, $J/(m^2 \cdot deg \cdot sec^{1/2})$	$n_1(t)$, $1/(m \cdot sec^{-1}/_2)$	$m_2(t)$, $J/(m^2 \cdot deg \cdot sec^{-1/2})$	$n_2(t)$, $J/(m^2 \cdot deg \cdot sec^{-1/2})$
0	1180,3	647,87	2172,7	—353114,5
10	887,9	1159,14	5455,1	—2991399,0
20	843,2	1232,66	9195,7	—7597691,0
30	835,3	1242,94	57080,4	—69604584,0
40	835,3	1239,50	—9041,4	16367026,5
50	846,8	1217,66	—3074,0	8648101,4
100	904,5	1107,36	648,3	3621020,9
150	967,3	990,04	1114,2	2942264,2
200	1033,0	864,19	1195,1	3083090,8
250	1231,7	515,13	1273,5	2584737,4
300	1173,0	586,77	1065,6	4737377,8

As is easy to note from Table 1, the thermal activity coefficient of water has a kind of change similar to the change in the heat conductivity coefficient of water in the $\varkappa$, t coordinate system, and hence the maximum $\varkappa$ are not located around 140°C on the isobars but approximately around 100°C.

For $pv = RT$ and $\varkappa = \varkappa'_s$, we will have from (2) and (3)

$$-\frac{B}{E} = \rho_s^3 \tag{4}$$

and

$$-\frac{B_\varkappa}{E_\varkappa} = \rho_s^3. \tag{5}$$

The validity of the proposed equation (3) is verified by the linearity of the complex $\varkappa/\varkappa'_s - 1/\rho$ as a function of ρ^3 on the 0; 50; 100; 150; 200 and 250°C isotherms, represented as follows:

$$\frac{\frac{\varkappa}{\varkappa'_s} - 1}{\rho} = B_\varkappa + E_\varkappa \rho^3.$$

The coefficients $B_\varkappa$ and $E_\varkappa$ in (3), evaluated for the six isotherms mentioned in conformity with the relationship (3') by using two points corresponding to the pressures p_s and 500 bar, are presented in Table 2 and in Fig. 1. As is seen from (3), the dimensionality of these coefficients depends on the dimensionality of ρ, which we have expressed in g/cm^3.

As is seen from Fig. 1, the characteristic anomaly inherent to water is reflected in the coefficients $B_\varkappa$ and $E_\varkappa$ in the 0-50°C band. In order to establish the behavior of their variation in this range, values of $B_\varkappa$ and $E_\varkappa$ must be determined taking account of the data on ρ and c_p at 10, 20, 30 and 40°C in [7]. Taking account of this singularity, as well as the existing relationship between the coefficients $B_\varkappa$ and $E_\varkappa$ according to (5), it would be sufficient to approximate one of them, i.e., $B_\varkappa$ which has a relatively simple outline, where it would be approximated by parts

$$\text{between } 0 \text{ and } 50^\circ\text{C} \quad B_\varkappa = \sum_0^5 b_i t^i, \tag{6}$$

where $b_0 = -2130200 \cdot 10^{-7}$; $b_1 = -3242968 \cdot 10^{-8}$; $b_2 = -2217562 \cdot 10^{-9}$; $b_3 = -7427125 \cdot 10^{-11}$; $b_4 = 1211375 \cdot 10^{-12}$; $b_5 = -7619167 \cdot 10^{-15}$,

$$\text{between } 50 \text{ and } 250^\circ\text{C} \quad B_\varkappa = (B_\varkappa)_{t=50} + b(t - 50), \tag{7}$$

where $(B_\varkappa)_{t=50} = -0.38440$; $b = 0.0010495$.

The results calculated from (1) and (3) are compared in Table 1. As is seen from this table, the formula (3) proposed describes the thermal activity coefficient of water exceptionally well even upon extrapolating the formula to 300°C.

It has been established in [8-11] that the heat conductivity and viscosity coefficients of water are also expressed in a form analogous to the equation of state, i.e.,

TABLE 4. Comparison Between the Values of the Thermal Activity Coefficient of Water $\varkappa$(J/m^2 · deg · sec$^{1/2}$) Calculated by Means of (1) (first row), (12) (second row), and (13) (third row)

p, bar	By the formula	$\varkappa$ at the temperature, °C						
		0	50	100	150	200	250	300
p_s	(1)	1548,9	1629,8	1657,5	1646,5	1606,8	1549,5	1489,9
	(12)	1548,9	1625,7	1657,5	1646,5	1606,8	1549,5	—
	(13)	1553,9	1630,6	1658,6	1646,7	1607,6	1550,1	—
50	(1)	1551,5	1634,5	1662,2	1650,7	1610,4	1550,1	—
	(12)	1551,5	1634,6	1661,9	1650,4	1610,3	1550,0	—
	(13)	1554,8	1639,2	1662,2	1649,7	1611,3	1550,1	—
100	(1)	1554,0	1638,9	1666,8	1653,9	1613,7	1558,2	1491,2
	(12)	1554,1	1639,5	1666,4	1653,4	1613,7	1553,7	1492,8
	(13)	1554,8	1639,2	1665,8	1652,6	1614,4	1552,7	1494,3
300	(1)	1564,1	1656,5	1682,1	1668,4	1629,8	1572,3	1504,6
	(12)	1563,8	1657,8	1680,8	1666,3	1628,4	1567,6	1520,4
	(13)	1558,3	1656,5	1680,3	1667,3	1626,7	1565,6	1518,0
500	(1)	1574,1	1670,6	1694,4	1684,1	1644,8	1588,7	1520,6
	(12)	1572,9	1672,4	1694,0	1680,1	1641,4	1577,3	1538,0
	(13)	1565,3	1673,8	1694,8	1679,1	1642,1	1578,5	1544,1
800	(1)	1592,6	1692,8	1722,6	1713,9	1677,6	1619,3	1545,3
	(12)	1588,5	1694,3	1718,4	1705,9	1667,3	1593,3	1556,7
	(13)	1583,3	1701,5	1718,7	1698,5	1663,1	1598,1	1587,2
1000	(1)	1600,7	1709,3	1738,1	1730,0	1696,3	1640,4	1570,7
	(12)	1598,2	1710,1	1732,8	1719,7	1682,0	1603,6	1571,4
	(13)	1599,1	1717,9	1733,2	1710,9	1676,4	1609,5	1608,5

$$\frac{\lambda}{\lambda_s'} = 1 + B_\lambda \rho + E_\lambda \rho^4, \tag{8}$$

$$\frac{\eta}{\eta_s'} = 1 + B_\eta \rho + E_\eta \rho^4. \tag{9}$$

Values of the coefficients B_λ, E_λ and B_η, E_η for water are presented in [9, 11].

For $\lambda = \lambda_s'$ and $\eta = \eta_s'$ it follows from (8) and (9)

$$-\frac{B_\lambda}{E_\lambda} = -\frac{B_\eta}{E_\eta} = \rho_s^3$$

or taking account of (5), we will have

$$-\frac{B_\varkappa}{E_\varkappa} = -\frac{B_\lambda}{E_\lambda} = -\frac{B_\eta}{E_\eta} = \rho_s^3. \tag{10}$$

According to (3), (8) and (9), the relationship between the thermal activity, heat conductivity and viscosity of water is expressed as follows by taking account of (10):

$$\frac{\frac{\varkappa}{\varkappa_s'} - 1}{E_\varkappa} = \frac{\frac{\lambda}{\lambda_s'} - 1}{E_\lambda} = \frac{\frac{\eta}{\eta_s'} - 1}{E_\eta}. \tag{11}$$

This formula (11) permits establishment of the following linear dependences between the thermal activity, heat conductivity, and also the viscosity coefficients of water

$$\varkappa = m_1(t) + n_1(t) \cdot \lambda, \tag{12}$$

$$\varkappa = m_2(t) + n_2(t) \cdot \eta, \tag{13}$$

where

$$m_1(t) = \varkappa_s' \left(1 - \frac{E_\varkappa}{E_\lambda}\right); \quad n_1(t) = \frac{E_\varkappa}{E_\lambda} \cdot \frac{\varkappa_s'}{\lambda_s'};$$

$$m_2(t) = \varkappa_s' \left(1 - \frac{E_\varkappa}{E_\eta}\right); \quad n_2(t) = \frac{E_\varkappa}{E_\eta} \cdot \frac{\varkappa_s'}{\eta_s'}.$$

Values of the coefficients $m_1(t)$, $n_1(t)$ and $m_2(t)$, $n_2(t)$ for each isotherm can be calculated either from these formulas or from two points in the linear dependences (12) and (13). Tabulated values of m(t) and n(t) relating λ to η [10] can also be used to evaluate these coefficients.

Values of these coefficients for water as calculated by the formulas presented above are presented in Table 3.

The validity of the dependences (12) and (13) obtained is confirmed by Fig. 2 and Table 4. Presented in this same table are values of the thermal activity coefficient for water at pressures up to 1000 bar. The values of λ and η from [9, 11] are hence used. Comparison between the results in the table shows that the method proposed for finding the thermal activity coefficient of water can successfully be used in the 0-300°C temperature and p_s to 1000 bar pressure ranges, where a small discrepancy relative to (1) is obtained only at 300°C.

It must be noted that the proposed dependences (3), (12) and (13) are of great practical value since they permit the establishment of connected thermophysical parameters of fluids on the one hand, and clarification of how accurate are the values used for the transport properties obtained by any experimental method.

In conclusion, it should be noted that deductions are made for fluids in general according to the results obtained herein for water as an example. As is seen from the exposition above, these deductions are based on the assumptions that the thermal activity coefficient and the transport properties of the fluid are expressed by equations similar to the equation of state. If the assumption concerning the fluid transport properties can be considered proved [9, 11], then the correctness of the assumption about the thermal activity coefficient, verified for water as an example, needs experimental confirmation for other fluids.

NOTATION

p, pressure; v, specific volume; ρ, density; ρ_s, saturated fluid density; ρ_0, fluid density for $pv/RT = 1$; R, gas constant; T, absolute temperature; B, B_λ, B_η, $B_\varkappa$ and E, E_λ, E_η, $E_\varkappa$, coefficients of the temperature function; $\varkappa$, fluid thermal activity coefficient; λ, heat conductivity coefficient; η, dynamic viscosity coefficient; $\varkappa_s'$, λ_s', η_s', the same quantities in the saturated state; c_p, isobaric specific heat.

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