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# THERMODYNAMIC PROPERTIES OF A FLUID AT HIGH PRESSURES

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*We present formulas for the thermal coefficients of a fluid at high pressures. The formulas are obtained on the basis of the Tate equation of state.*

In [1] equations were derived on the basis of the Tate equation of state for determining the thermodynamic properties of a fluid at high pressures. However, in formula (4) for the coefficient of volumetric expansion an error was made, as a result of which many ensuing expressions and statements about the change of sign of the thermal coefficients of pressure and volumetric expansion of water at a temperature of about 50°C were incorrect.

In [1] the properties of the fluid are described by the Tate equation in the form

$$\frac{p_0 + L(T)}{p + L(T)} = \left(\frac{v}{v_0}\right)^n , \tag{1}$$

where $n = \text{const}$. In [2, 3] for liquids and dense gases a more general equation was applied:

$$\frac{p_0 + B(T)}{p + B(T)} = \left(\frac{v}{v_0}\right)^{n(T)} . \tag{2}$$

The elastic pressure $B$ [4] and exponent $n$ are determined from experimental or standard reference data. For example, for water under pressures of from 0.1 to 1000 MPa, the values of $n$ and $B$ from [6] and the maximum relative error $\delta = |v_{\text{cal}} - v_{\text{tab}}|/v_{\text{tab}}$ in calculations by Eq. (2) are presented in Table 1. For a given temperature $T$ from the known values of $v_{\text{tab}}$ at three values of $p$ the exponent $n$ and pressure $B$ were determined from the relations

$$\frac{p_2 - p_0}{p_2 - p_1}\left(\frac{v_0}{v_1}\right)^n - \frac{p_1 - p_0}{p_2 - p_1}\left(\frac{v_0}{v_2}\right)^n = 1 ;$$

$$B = \left[p_2 - p_0\left(\frac{v_0}{v_2}\right)^n\right] \Big/ \left[\left(\frac{v_0}{v_2}\right)^n - 1\right] .$$

Equation (2) not only presents with good accuracy the data on the compressibility of liquids and dense gases but also makes it possible to perform extensive pressure extrapolation. For example, if for water we consider the values of specific volumes at pressures from 0.1 to 10 MPa to be known, we can determine the approximate values of $n$ and $B$ and find the values of specific volumes at pressures $p = 100$, $500$, $p_{\max}$, for which the values of $v$ are known [5]. The results of such calculations are presented in Table 2.

It is seen from the table that at pressures that exceed by factors of 10, 50, and 100 the greatest pressure at which a specific volume of water is known, $\delta$ does not exceed 0.17, 1.65, 3.2%, respectively. Similar results were obtained for a number of hydrocarbons and nitrogen [2, 3].

The thermal coefficients of a fluid that obeys Eq. (2) are determined from the following formulas: for the isothermal coefficient of compression

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TABLE 1. Parameter Values and Maximum Relative Error of Eq. (2) for Water

| Parameters | 0 | 25 | 50 | 75 | 100 |
|---|---|---|---|---|---|
| $n$ | 7.554 | 5.559 | 5.825 | 6.049 | 5.920 |
| $B$, MPa | 243.27 | 414.68 | 394.85 | 365.55 | 357.80 |
| $\delta$, % | 0.10 | 0.10 | 0.06 | 0.02 | 0.10 |

TABLE 2. Parameter Values and Maximum Relative Error of Eq. (2) for Water for Known Specific Volume at the Pressures of from 0.1 to 10 MPa

| Parameters | 0 | 25 | 50 | 75 | 100 |
|---|---|---|---|---|---|
| $n$ | 5.0 | 4.5 | 4.5 | 4.5 | 4.5 |
| $B$, MPa | 391.15 | 494.83 | 504.07 | 487.52 | 456.44 |
| $\delta_{100}$, % | 0.10 | 0.07 | 0.11 | 0.14 | 0.17 |
| $\delta_{500}$, % | 1.70 | 1.31 | 1.26 | 1.43 | 1.65 |
| $\delta_{p_{\max}}$, % | 2.33 | 2.25 | 2.59 | 2.96 | 3.20 |
| $p_{\max}$, MPa | 650 | 900 | 1000 | 1000 | 1000 |

TABLE 3. Isobaric Coefficient of Volumetric Expansion $\beta \cdot 10^4$ K$^{-1}$

| $t$, °C | $p$, MPa | | | |
|---|---|---|---|---|
| | 0.1 | 50 | 100 | 500 |
| 0 | −0.852 | 0.837 | 1.57 | 2.6 |
| 20 | 2.07 | 2.78 | 3.41 | 3.65 |
| 40 | 3.89 | 3.99 | 4.18 | 4.25 |
| 60 | 5.29 | 5.02 | 4.89 | 4.55 |
| 80 | 6.47 | 5.94 | 5.58 | 4.7 |

$$\alpha = -\frac{1}{v}(\partial v/\partial p)_T = \frac{1}{n(p+B)}; \tag{3}$$

the isobaric coefficient of volumetric expansion

$$\beta = \frac{1}{v}(\partial v/\partial T)_p = \beta_0 + \frac{p-p_0}{n(p_0+B)(p+B)}\frac{dB}{dT} + \frac{1}{n^2}\ln\left(\frac{p+B}{p_0+B}\right)\frac{dn}{dT}; \tag{4}$$

the thermal coefficient of pressure

$$\gamma = \frac{1}{p}(\partial p/\partial T)_v = \frac{\beta_0}{\alpha p} + \frac{p-p_0}{p(p_0+B)}\frac{dB}{dT} + \frac{1}{\alpha p n^2}\ln\left(\frac{p+B}{p_0+B}\right)\frac{dn}{dT}. \tag{5}$$

When Eq. (1) ($dn/dT = 0$) is used, Eqs. (4) and (5) do not coincide with formulas (4) and (5) of [1], since they involve additional terms: $\beta_0$ in Eq. (4) and $\beta_0/\alpha p$ in Eq. (5). The values of the isobaric coefficient of the volumetric expansion of water determined according to [5-7] are given in Table 3.

In [1] it is claimed that water has a certain critical temperature ≈ 50°C, in transition through which the coefficients $\beta$ and $\gamma$ change their sign. From Eqs. (4), and (5), Table 3, and [6] it follows that at a temperature of 50°C the coefficients $\beta$ and $\gamma$ remain positive, but with an increase in pressure for $t < 50$°C the coefficient $\beta$ increases, whereas for $t > 50$°C it decreases.

In Fig. 1 of [1] the density scale is shifted along the ordinate axis. Since the density of water at $p = 0.1$ MPa is equal to 1000 kg/m$^3$, then instead of 980, 1000, and 1020 we should have the numbers 990, 1010, and 1030, respectively. In contrast to [1], the change in the isobaric heat capacity $\Delta c_p$ with an increase in pressure is not always much smaller than $c_{p0}$. According to [7], for water the ratio $c_p/c_{p0}$ at $t = 0$ and 20°C is equal to 0.901 and 0.949, respectively.

**Conclusions.** Equation (2) not only describes with good accuracy the volumetric behavior of fluids but also allows one to carry out extensive extrapolation with respect to pressure. The formulas used in [1] for calculating the thermodynamic parameters of a fluid at a high pressure and the mathematical model of heat and mass transfer in melting and crystallization of a substance need correction.

## NOTATION

$v$, specific volume of fluid; $p$, pressure; $T$, temperature; $n$, isotherm index; $B$, parameter; $\alpha$, isothermal coefficient of compression; $\beta$, isobaric coefficient of volumetric expansion; $\gamma$, thermal coefficient of pressure; $c_p$, specific isobaric heat capacity; $t$, temperature, °C; $v_0$, $\beta_0$, $c_{p0}$, values of respective quantities at the initial pressure $p_0$.

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