SATURATION CURVE EQUATIONS FOR NORMAL AND HEAVY WATER

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Compact and precise equations are obtained for the saturation curves of normal and heavy water.

At the present time a large number of equationsof state have been proposed for the saturation pressure of conventional water, differing in their complexity and accuracy. In [1] an analysis using a special algorithm was employed to obtain an equation which described the original data with a minimal number of terms. But new more precise measurements were then performed of saturated vapor pressure at the triple point [2], as a result of which a new value was obtained, differing from that used previously in all the equations. New data has also appeared for the low-temperature range. The estimates of the water vapor critical parameters have also changed somewhat. These facts make construction of a new equation desirable.

For initial data we will employ the triple point pressure value of [2], the data of [3] for 0-100°C, which not only agree well with experimental results, but permit thermodynamic correlation with other properties, the results of [4] for 100-360°C, these being the basis of the MST-63 international tables [5], and the data of [6] for temperatures of 360-374°C. Critical parameter values were taken from [7]. The equation obtained has a form similar to the equation [1]

$$\ln\frac{p}{p_c}=\Theta^{-1}(a_1\tau+a_2\tau^{1.5}+a_3\tau^{2.5}+a_4\tau^{6.5}+a_5\tau^{7.5}),\qquad(1)$$

with coefficients presented in Table 1. The triple-point pressure given by Eq. (1) is 611.657 Pa, which agrees with the experimental value (611.657 ± 0.010 Pa) within the experimental uncertainty, and reproduces atmospheric pressure (101,325 Pa) exactly at t = 100°C. Over almost the entire range the calculated data diverges from the initial by not more than 0.01%, which is several times less than the uncertainty established for MST-63, only reaching 0.018% near 20°C.

The good results obtained with Eq. (1) for normal water make it possible to construct a similar equation for heavy water. To do this, the available experimental studies on measurement of heavy water saturation pressure were analyzed, and a set of initial data containing the most reliable results was compiled. Values obtained in [8-13] were used. All experimental pressure values were recalculated to a 100% D_2O concentration using Raule's law. The D_2O critical parameter values were taken from [14].

It should be noted that the accuracy of the experimental pressure values at low temperatures for heavy water is much worse than for normal water. Thus, e.g., the data of [10] near 20°C have a scattering of tenths of a percent, while with decrease in temperature the scattering reaches values greater than 1%. The divergence in [10] and [11] is of the same order. Under these conditions it is useful to consider certain thermodynamic principles to establish the correct behavior of the equation at low temperatures. As is well known, for the low-pressure range it is true that

$$\frac{dr}{dT}=c_p^0-c_s'.\qquad(2)$$

On the other hand, from the Clausius—Clayperon equation, neglecting the volume of the liquid phase and assuming that the vapor obeys the ideal gas law, we find

$$\frac{dr}{dT}=\frac{d^2p}{dT^2}Tv+2v\frac{dp}{dT}-\frac{RT^2}{p}\left(\frac{dp}{dT}\right)^2.\qquad(3)$$

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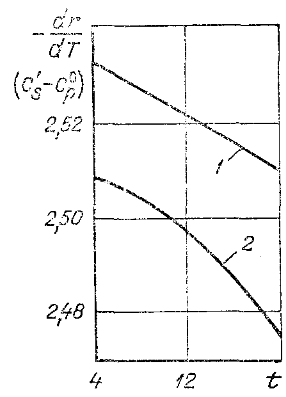

Fig. 1. Change in thermodynamic quantities in low temperature range: 1) ($c_s' - c_p^0$); 2) dr/dT. t, °C; ($c_s' - c_p^0$) and dr/dT, kJ/kg.

TABLE 1. Coefficients of Eq. (1)

Coefficient	H_2O	D_2O
a_1	—7,86529984	—7,93576835
a_2	1,89960784	1,89857357
a_3	—2,37217403	—2,57815673
a_4	—9,74439186	—11,2412899
a_5	9,72654391	10,5606232
T_c (MPTSh-68)	647,073	643,887
p_c, MPa	22,0477	21,659

TABLE 2. Heavy Water Saturated Vapor Pressure

t, °C	p, MPa	t, °C	p, MPa	t, °C	p, MPa
3,82	0,00066087	130	0,26144	260	4,7226
10	0,0010261	140	0,35154	270	5,5468
20	0,0019986	150	0,46516	280	6,4764
30	0,0037005	160	0,60649	290	7,5207
40	0,0065469	170	0,78011	300	8,6892
50	0,0111175	180	0,99093	310	9,9925
60	0,018194	190	1,2443	320	11,442
70	0,028795	200	1,5457	330	13,052
80	0,044212	210	1,9013	340	14,836
90	0,066043	220	2,3172	350	16,813
100	0,096215	230	2,8002	360	19,009
110	0,13701	240	3,3572	370	21,465
120	0,19107	250	3,9954	370,74	21,659

On the right-hand side of Eq. (3) the major role is played by the first term, and the character of the change in dr/dT with decrease in temperature is determined mainly by the change in the second derivative d^2p/dT^2. Therefore, from a set of equations of the form of Eq. (1), obtained with various statistical weights for the experimental saturation pressure values, an equation was chosen for which with reduction in temperature the derivative calculated with Eq. (2) tends to $c_p^0 - c_s'$ (Fig. 1). To calculate the latter, an equation for c_p^0 from [15] and an equation for liquid heat capacity from [16] were used.

The coefficients of Eq. (1) for heavy water are presented in Table 1, and the calculated saturation pressure values from this equation are given in Table 2.

The divergence between the tabular data and experimentally measured pressures is within the uncertainty of the latter over the entire temperature interval. Thus, an equation of the form of Eq. (1) ensures satisfactory description of the original data over the entire range from the triple to the critical point, with a minimum number of terms.

NOTATION

p, saturated vapor pressure; p_c, critical pressure; T, absolute temperature; T_c, critical temperature; $\Theta = T/T_c$, dimensionless temperature; $\tau = 1 - \Theta$; r, heat of vaporization; c_p^o, isobaric heat capacity of vapor in ideal gas state; c_s', liquid heat capacity along saturation curve; v, specific volume of vapor; a_i, coefficients of Eq. (1).

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