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EQUATION TO COMPUTE THE SATURATED VAPOR PRESSURE ON THE BASIS OF THE PRINCIPLE OF CORRESPONDING STATES

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A generalized equation is developed for the saturated vapor pressure computation of individual substances. The integral error of the computed data is within 1-3%.

The most effective approaches for the computation of the thermodynamic properties of substances are based on application of the principle of corresponding states (PCS). It is known that substances for which the intermolecular interaction is described by spherically symmetric pairwise additive potential are called simple. They are subject to a simple PCS in which two governing parameters are sufficient for determination of the properties. If the substance behavior deviates from the simple PCS, one, two, or more correlation factors are introduced.

It is sufficient to use just one correlation factor for normal (non-associated) substances. Then the equation for the saturated vapor pressure of such substances is written in the form

$$P_R = P_R(T_R, A), \quad (1)$$

where $P_R = P/P_C$ and $T_R = T/T_C$ are the pressure and temperature referred to the critical values, and A is the correlation factor. Let us note that the correlation factors determined on the basis of the dependences of P_R and T_R on the saturation line are utilized successfully in a single-phase domain also. In order to find the explicit form of A it is necessary to have an analytic expression for the temperature dependence of the saturated vapor pressure with one correlation factor. An approximate exponential Boltzmann formula was used in [1] by reducing it to the dimensionless form

$$\ln P_R = S\left(1 - \frac{1}{T_R}\right) + \ln T_R. \quad (2)$$

Knowledge of a single point on the saturation line is sufficient for finding the numerical value of S of a specific substance.

The normal boiling point is chosen for determination of the value S since, as a rule, it is known with higher accuracy than any other point on the saturation line. Consequently, the correlation factor is

$$S = \frac{\ln (P_{RB}/T_{RB})}{1 - \frac{1}{T_{RB}}}, \quad (3)$$

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TABLE 1. Results of Comparing the Computed Values Obtained by Means of (4)-(7) with Data on the Saturated Vapor Pressure [3] for the Low-Temperature Domain

Substance	Temperature range, T_R	R.M.S. deviation, % from the equations			
		(4), (5)	(5), (6)	(4), (7)	(6), (7)
Propane	0,45—0,67	0,59	0,90	0,48	0,36
Isobutane	0,63—0,66	0,01	0,15	0,00	0,00
Trans-butene-2	0,47—0,64	1,11	0,63	0,23	0,54
2-Methyl propene	0,52—0,65	1,14	0,86	0,93	0,87
Butadiene-1,3	0,46—0,64	0,86	2,03	0,48	0,58
Isopropyl benzen	0,54—0,68	2,61	4,86	0,17	0,46
Chlorbenzene	0,53—0,64	2,04	3,01	0,17	0,29
Isobutyric aldehyde	0,56—0,65	0,67	0,86	0,40	0,29
Propanone-2	0,59—0,65	0,50	0,41	0,47	0,47
Methanal	0,40—0,61	8,51	7,64	2,70	2,46
Ethanal	0,59—0,67	1,14	1,05	1,11	1,11
Propanol	0,62—0,70	5,72	6,58	0,37	0,50
2-Methyl propanol-2	0,66—0,72	4,68	5,24	0,24	0,20
Butanol-1	0,64—0,71	5,38	5,75	0,50	0,56
Ethanol acid	0,51—0,67	1,98	0,50	0,91	0,64
Phenol	0,55—0,66	8,66	10,38	0,37	0,21
Averages		2,9	3,1	0,6	0,6

where $P_{RB} = 0.10132/P_C$, P_C[MPa], $T_{RB} = T_B/T_C$.

Equation (2) yields noticeable discrepancies with experiment in the low-temperature range on the coexistence curve for $T_R < 0.6$. Consequently, a correction function $f(\delta)$ compensating for these discrepancies is introduced in [1] for (2):

$$f(\delta) = A_1\delta + A_2\delta^2 + A_3\delta^3 + A_4\delta^4 + A_5\delta^5, \tag{4}$$

where $\delta = T_R - T_{RB}$; $A_1 = 0.75564$, $A_2 = -5.51179$; $A_3 = 18.442$; $A_4 = -46.0427$; $A_5 = 58.8$, then

$$\ln P_R = S\left(1 - \frac{1}{T_R}\right) + \ln T_R + f(\delta). \tag{5}$$

When using the normal boiling temperature (5) goes over into (3). The main disadvantage of this equation is that it does not assure the passage to the limit at the critical point. The problem of obtaining a correction function $f(\delta)$ in a form assuring the passage to the limit in (3) for $T_R = T_{RB}$ and the passage to the limit at the critical point is posed in this paper. To do this we represent the correction function in the form

$$f(\delta) = (T_R - 1)(A_1\delta + A_2\delta^2 + A_3\delta^3 + A_4\delta^4 + A_5\delta^5), \tag{6}$$

where $A_1 = 2.0389$, $A_2 = 12.6568$, $A_3 = 18.579$, $A_4 = -49.2763$, $A_5 = 749.561$ are determined by a linear approximation method from reliable data on propane [2]. Propane is selected since there are skeleton data along the whole saturation curve for it and the reduced temperature of the triple point has the least value (0.23) as compared with other well-studied substances. In principle, reliable data on any other substance or set of substances could be used to determine the coefficients of the correction function (6) since no parameters characterizing a specific substance are in this function while the coefficients are universal.

In the presence of a low-temperature point (P_1 or T_1) a correction factor K is introduced ahead of the function f in (5)

$$\ln P_R = S\left(1 - \frac{1}{T_R}\right) + \ln T_R + (1 + K)f, \tag{7}$$

where

$$K = \frac{\ln P_{R1} - S\left(1 - \frac{1}{T_{R1}}\right) - \ln T_{R1}}{f} - 1.$$

TABLE 2. Results of Comparing Computed Values Obtained by Means of (4)-(7) with Data on the Saturated Vapor Pressure in the Range between the Triple and Critical Points

Substance	R.M.S. deviation, % from the equations				Source
	(4), (5)	(5), (6)	(4), (7)	(6), (7)	
Methane	1,20	1,91	0,41	0,65	[4]
Ethane	3,13	2,41	0,48	0,90	[5]
Propane	2,02	2,81	1,64	0,94	[2]
Isobutane	3,57	6,06	1,31	1,84	[6]
Cyclohexane	1,43	1,50	0,98	0,49	[7]
Ethylene	3,09	3,21	2,16	2,07	[8]
Nitrogen	1,12	1,21	0,34	0,42	[9]
Methanol	5,17	2,30	2,82	2,15	[10]
Water	8,86	7,86	3,75	3,60	[11]
Averages	3,3	3,2	1,6	1,4	

It should be noted that K has the meaning of an additional correlation factor. Equations (5) and (7) with the correction functions (4) and (6) were verified by means of reliable data on the saturated vapor pressure of polar and nonpolar substances. The results are represented in Table 1 and 2.

Results of comparing the computed values obtained from (4)-(7) with saturated vapor pressure data generalized in [3] for representatives of different homological series of hydrocarbons and organic substances for the low-temperature domain are presented in Table 1. It is known that the methods of determining the saturated vapor pressure for the low-temperature domain assure a significantly greater error in computation than for the high-temperature domain. Consequently, it is customary to examine these domains separately in the literature. Results of comparing computed values with data about the saturated vapor pressure between the triple and critical points are presented in Table 2. Representatives of different classes of substances are selected for which there are skeleton tables in the literature.

Results of the comparison showed that in the presence of the normal boiling temperature and critical temperatures and pressures, the integral error of the computed data should be estimated at 3% although it has lower values for hydrocarbons. But the error can exceed the integral value for polar, associated substances.

Utilization of the obtained correction function (6) assures the same computation error as the function (4) but yields the passage to the limit of (7) at the critical point.

The proposed equation (5), (6) can be among the group of such three-parameter equations as the Lee–Kessler, Rydell, Rydell–Planck–Miller, et al., [12]. The initial information T_B, T_C and P_C is required for its utilization.

The listed equations are not recommended in [12] for utilization in the low-temperature domain ($P_S < 1$ kPa) while (5), (6) assure reliability of the computation to the triple point. The errors in the calculated values according to the equations mentioned are commensurate but insertion of the additional correlation factor K in (7) reduces the computation error by more than two times.

The developed equation with the new correlation factors introduced S (Eq. (3)) and K (Eq. (7)) permits reliable determination of the saturated vapor pressure of polar and nonpolar substances in the interval between the triple and critical points.

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