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THERMODYNAMIC PROPERTIES OF n-BUTANE

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Equations are derived and used to calculate a table of thermodynamic properties of n-butane in the saturated state.

In calculating chemical engineering processes and refrigeration equipment cycles in which n-butane is used as the raw material or cooling agent, reliable data on the thermodynamic properties of that material are essential.

Below we will present self-consistent equations for pressure, density, specific heat, heat of evaporation, enthalpy, and entropy, which were obtained by critical evaluation of experimental data. The equations were used to calculate a table of thermodynamic properties for n-butane in the saturated state, suitable for practical use.

Saturated vapor pressure was calculated with the equation

$$\lg p = A + BT^{-1} + CT + DT^2 + ET^3 + KT^4, \tag{1}$$

which to an accuracy of $\pm 0.2\%$ describes the experimental data of [1-4] on saturated vapor pressure of n-butane over the temperature range from the triple point to the critical point. In Eq. (1) pressure is expressed in MPa and temperature in °K.

The constants appearing in Eq. (1) were determined by the method of least squares: $A = 13.9878$; $B = -3597.20$; $C = -8.05251 \cdot 10^{-3}$; $D = -3.05786 \cdot 10^{-5}$; $E = 8 \cdot 13812 \cdot 10^{-8}$; $K = -4.57782 \cdot 10^{-11}$.

Density of the boiling (saturated) liquid has been measured over the following ranges: [5] (273-32°K); [6] (293-306°K); [7] (294-394°K); [2] (325-422°K); [8] (227-333°K); [9] (135-275°K); [10] (93-173°K); [11] (135-300°K); [12] (283-368°K); [13] (at 293 and 298°K); [14] (311-411°K); [15] (at 288.65 and 327.55°K). The data of [9-12] are the most reliable and precise.

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The empirical equation

$$\rho' = \rho_{cr} + \sum_{i=1}^{i=5} a_i (T_{cr} - T)^{i/3} \tag{2}$$

was obtained, which over the temperature range from the triple point to the critical point reproduces the data of [2, 9-12] on density of the boiling liquid as a function of absolute temperature within an accuracy of $\pm 0.2\%$.

In Eq. (2) the density ρ' is expressed in kg/m^3, T in °K, $\rho_{cr} = 225$ kg/m^3, and $T_{cr} = 425.16$°K. The constants a_i were determined from experimental density values of [2, 9-12] by the method of least squares: $a_1 = 5.08858 \cdot 10^1$; $a_2 = 5.61326$; $a_3 = -7.06208 \cdot 10^{-1}$; $a_4 = 4.28509 \cdot 10^{-2}$; $a_5 = 3.84935 \cdot 10^{-3}$.

The density of the dry saturated vapor has been measured over the following ranges: 273-329°K [5]; 289-390°K [7]; 283-368°K [12]. The most reliable and accurate data are those of [12]. Tabular values of density ρ'' were calculated using the Clayperon–Clausius equation

$$r = T\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right)\frac{dp}{dT}. \tag{3}$$

Heat of evaporation was determined from the following data: 275-297°K [5]; 293-389°K [7]; at T = 272.66°K [3]. The equation

$$r = \sum_{i=1}^{i=4} C_i (T_{cr} - T)^{i/3} \tag{4}$$

was obtained, with coefficients C_i obtained from heat of evaporation data from [3, 5]: $C_1 = 41.7969$; $C_2 = 11.3498$; $C_3 = -1.00585$; $C_4 = -1.02924 \cdot 10^{-2}$.

The specific heat of the boiling liquid c_s' has been measured as follows: 257-294°K [5]; 12-273°K [3]; 140-262°K [18]. The specific heat of the vapor at atmospheric pressure $c_p \approx c_p^0$ was measured in [7] (305-433°K). This value diverges from the c_p^0 data of [16, 17], calculated from molecular spectra. Data from [3, 5, 18 and 16, 17] were used to generate an equation for specific heat of the boiling liquid c_s' and specific heat of butane in the ideal gas state c_p^0:

$$\begin{aligned} c_s' &= 2.82667 - 1.39455 \cdot 10^{-2}T + 7.18344 \cdot 10^{-5}T^2 - 1.20651 \cdot 10^{-7}T^3 + \\ &+ 1.55171 \cdot 10^{-11}T^4 + 2.00540 \cdot 10^{-13}T^5, \text{ kJ/(kg·deg K)}, \\ c_p^0 &= 9.42838 \cdot 10^{-2} + 6.04268 \cdot 10^{-3}T - 2.26393 \cdot 10^{-6}T^2 - \\ &- 1.93833 \cdot 10^{-10}T^3 + 2.31758 \cdot 10^{-13}T^4, \text{ kJ/(kg·deg K)}. \end{aligned} \tag{5}$$

The enthalpy of the boiling liquid H' was calculated with the equation

$$H' = H_0' + \int_{273.15}^{T} c_s' dT + \int_{273.15}^{T} \frac{1}{\rho'}\left(\frac{dp}{dT}\right)_s dT, \tag{6}$$

in which the enthalpy of the boiling liquid H_0' at T = 273.15°K was taken equal to 500 kJ/kg, c_s' and ρ' were determined with Eqs. (5) and (2), and the derivative $(dp/dT)_s$ was found by differentiation of Eq. (1).

The enthalpy H" and entropy s" of the dry saturated vapor were determined with the equations

$$H'' = H' + r, \tag{7}$$

$$s'' = s' + r/T. \tag{8}$$

TABLE 1. Thermodynamic Properties of n-Butane in the Saturated State

T, K	p, 10^5 Pa	ρ', kg/m^3	ρ'', kg/m^3	H', kJ/kg	H'', kJ/kg	r, kJ/kg	s', kJ/kg·deg K	s'', kJ/kg·deg K
210	0,0402	664,5	0,137	362,8	791,1	428,3	1,430	3,470
215	0,0564	659,7	0,188	373,2	798,6	425,4	1,479	3,458
220	0,0779	654,8	0,254	383,6	806,1	422,5	1,527	3,447
225	0,1056	650,0	0,337	394,1	813,5	419,5	1,574	3,438
230	0,1412	645,0	0,441	404,6	821,0	416,3	1,620	3,421
235	0,1861	640,0	0,569	415,3	828,4	413,1	1,666	3,424
240	0,2420	635,0	0,726	426,0	835,9	409,8	1,712	3,419
245	0,3108	630,0	0,914	436,9	843,3	406,4	1,756	3,415
250	0,3946	624,8	1,139	447,8	850,7	402,9	1,801	3,412
255	0,4955	619,7	1,405	458,9	858,2	399,3	1,844	3,410
260	0,6159	614,5	1,718	470,1	865,6	395,5	1,888	3,409
265	0,7584	609,2	2,081	481,3	873,0	391,7	1,931	3,409
270	0,9255	603,9	2,507	492,7	880,4	387,7	1,973	3,409
275	1,1201	598,5	2,985	504,3	887,8	383,5	2,016	3,410
280	1,345	593,1	3,536	515,9	895,2	379,3	2,058	3,412
285	1,603	587,6	4,162	527,7	902,6	374,9	2,099	3,415
290	1,897	581,9	4,869	539,6	910,0	370,3	2,141	3,418
295	2,231	576,3	5,666	551,7	917,3	365,6	2,182	3,422
300	2,607	570,5	6,559	564,0	924,7	360,7	2,223	3,426
305	3,030	564,6	7,558	576,3	932,0	355,6	2,264	3,430
310	3,502	558,6	8,671	588,9	939,3	350,4	2,305	3,435
315	4,027	552,5	9,908	601,6	946,6	344,9	2,346	3,441
320	4,608	546,3	11,28	614,5	953,8	339,3	2,386	3,447
325	5,249	539,9	12,80	627,6	961,0	333,4	2,427	3,453
330	5,954	533,4	14,49	640,9	968,1	327,2	2,468	3,459
335	6,728	526,7	16,36	654,4	975,2	320,8	2,508	3,466
340	7,572	519,8	18,42	668,1	982,2	314,1	2,549	3,473
345	8,493	512,7	20,71	682,1	989,1	307,0	2,589	3,479
350	9,494	505,4	23,24	696,2	995,9	299,7	2,630	3,486
355	10,58	497,8	26,04	710,6	1002,5	291,9	2,671	3,493
360	11,75	489,9	29,16	725,3	1009,0	283,7	2,712	3,500
365	13,02	481,7	32,62	740,2	1015,3	275,1	2,753	3,507
370	14,39	473,2	36,49	755,4	1021,3	265,9	2,795	3,513
375	15,87	464,1	40,83	770,9	1027,0	256,1	2,837	3,519
380	17,45	454,6	45,71	786,6	1032,3	245,7	2,878	3,525
385	19,16	444,4	51,24	802,8	1037,2	234,4	2,920	3,529
390	20,98	433,5	57,55	819,2	1041,4	222,2	2,962	3,532
395	22,94	421,6	64,84	836,0	1044,7	208,8	3,005	3,534
400	25,03	408,5	73,36	853,1	1047,0	193,9	3,048	3,533
405	27,28	393,8	83,55	870,6	1047,6	177,0	3,092	3,529
410	29,67	376,6	96,13	888,6	1045,9	157,3	3,136	3,520
415	32,23	355,5	112,55	906,9	1040,2	133,3	3,180	3,502
420	34,97	326,5	136,7	925,7	1026,5	100,8	3,225	3,465
421	35,53	318,7	143,8	929,5	1021,8	92,3	3,234	3,454
422	36,11	309,75	151,5	933,4	1015,9	82,5	3,243	3,439
423	36,69	298,8	162,4	937,1	1007,9	70,8	3,252	3,420
424	37,29	283,9	175,0	941,0	996,3	55,3	3,262	3,395
425	37,88	254,2	202,3	944,9	970,8	25,9	3,271	3,332
425,16	37,98	225,0	225,0	945,5	945,5	0,0	3,272	3,272

NOTATION

T, temperature, °K; p, pressure, Pa (MPa); ρ, density, kg/m^3; H, enthalpy, kJ/kg; s, entropy, kJ/(kg·deg); r, heat of evaporation, kJ/kg; c_s' and c_p^o, specific heats of saturated liquid and ideal gas, kJ/(kg·deg). Single and double primes denote parameters of the boiling liquid and dry saturated vapor, respectively.

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THERMODYNAMIC PROPERTIES OF ETHANOL AT ATMOSPHERIC PRESSURE

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Published data on density, speed of sound, and isobaric specific heat in liquid ethanol are generalized, and the values of isochoric specific heat, adiabatic and isothermal compression coefficients, and enthalpy are calculated for the temperature range 159.05-351.44°K.

The thermodynamic properties of pure (absolute) ethanol at atmospheric pressure have been studied quite thoroughly. The accumulated experimental material was systematized and partially generalized in [1-7]. The generalization was accomplished in the form of recommended interpolation equations or data tables. As a rule, recommended values were provided for temperatures above 273°K. However, modern methods of constructing thermodynamic property tables for liquids, in particular, those based on data from acoustical measurements, require the representation of a number of thermodynamic properties (ρ, W, and C_p) at atmospheric pressure as analytic expressions. Presently available handbooks and monographs either lack such equations or offer ones limited to a narrow temperature range, which are furthermore insufficiently precise in a number of cases.

It is obvious that the accumulated experimental data on the properties of ethanol and the generalizations thereof are not exhaustive, since new experimental data has been published, which with consideration of previous material makes possible a refinement and generalization

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