

Analytical expressions are obtained for the temperature dependence of the isobaric specific heat of liquid methanol and the C_{11} - C_{18} N-alcohols at 293-583 K at atmospheric pressure.

It is well known that experimental determination of specific heat is beset with significant technological difficulties. In connection with this, it is important to consider computation methods for determining thermodynamic properties, one of which is based on use of the law of change in properties in homological series. Use of this method permits, first, interrelationship of properties of various materials within a homological series, and second, interpolation or, within reason, extrapolation to determine such properties for members of the series for which they are unknown. A similar approach was used earlier [1] to find density in the N-alcohol series.

The goal of the present study is to investigate behavior of isobaric specific heat at atmospheric pressure in the series of pure liquid saturated monatomic alcohols.

The specific heat C_p of these alcohols has not been sufficiently studied experimentally. The lower alcohols up to pentanol-1 have been studied most thoroughly, the higher ones, less so. The handbook [2] contains citations of experimental data on C_p of the alcohols with C_1 - C_{15} , C_{18} . It should be noted that this same handbook considers practically all the more reliable experimental data existing for C_p of alcohols with normal structure. For the alcohols with C_{16} , C_{17} , and those with a number of carbon atoms (N) greater than 18 information on C_p is practically absent from the literature.

The uncertainty of the measurements at atmospheric pressure for the alcohols C_1 - C_5 does not exceed 0.3%, with the exception of butanol-1, for which it comprises approximately 1% for $T > 322$ K. The specific heat of the higher alcohols (C_6 - C_{15} , C_{18}) has been measured with an uncertainty of the order of 1.0-2.5%.

An analytical generalization of experimental data on C_p for the alcohols C_2 - C_8 , C_{10} in the temperature range from the normal fusion point to the boiling point was performed in [1, 3-9]. The accuracy of the approximation oscillated depending on the temperature interval and number of the homolog, but lay in the limits 0.1-2.0%.

Preliminary processing of the available information was carried out in the coordinates C_p , N by graphing experimental points [2] for the alcohols C_7 - C_{15} , C_{18} and generalization results [1,3-9] for the alcohols C_3 - C_8 , C_{10} taken at identical temperatures in the range 293-583 K in 10 K steps. This construction revealed that the original CP data fitted a series of curves (isotherms) with a scattering not exceeding ± 0.2 , ± 0.5 , 0.7% for C_3 , C_4 , C_5 , and ± 1.2 % for C_6 - C_{11} , C_{13} , C_{14} , C_{18} . For the C_{12} and C_{15} alcohols the deviations lie in the range 2-4% and are of a systemic character (positive for C_{12}). Thus, the processing results indicate that in the normal alcohol series within the limits of the estimated uncertainties (1.0-2.5%) the initial data show a dependence of specific heat on number of carbon atoms in the alcohol molecule at constant temperature. Analysis of this dependence revealed that the curves are continuously decreasing curves convex in the direction of the N-axis. Analytical smoothing of the original data in the coordinates C_p , N was accomplished by power series. The internal consistency of C_p values calculated in this manner was tested by constructing atmospheric pressure isobars in the coordinates C_p , T. This is of special importance, since the function $C_p = f(T)$ for these alcohols is of a complex character. The scattering of values (taken at identical temperatures) relative to the smoothed curves for both graphs did not exceed 0.3%.

TABLE 1. Coefficients of Eq. (1)

Alcohol	a_0	a_1	a_2	a_3	a_4	a_5	Temp. interval, K
Methanol	2,786	-5,1901	5,7584	29,471	—	—	176—337
Undecanol-1	33,376	-413,191	2039,87	-4725,27	5221,61	-2216,94	293—513
Dodecanol-1	43,274	-534,623	2635,80	-6187,30	7010,79	-3089,73	303—533
Tridecanol-1	44,356	-546,727	2690,30	-6310,15	7145,50	-3145,80	313—553
Tetradecanol-1	26,370	-340,010	1747,54	-4176,73	4746,21	-2071,69	313—563
Pentadecanol-1	42,001	-526,527	2631,01	-6252,82	7163,85	-3187,22	323—583
Hexadecanol-1	22,396	-313,331	1714,97	-4308,90	5124,66	-2340,56	333—583
Heptadecanol-1	-24,176	206,491	-582,30	717,10	-322,25	—	333—583
Octadecanol-1	-48,906	472,034	-1711,57	3094,86	-2802,55	1025,83	343—583

TABLE 2. Isobaric Specific Heat of Liquid Methanol at Atmospheric Pressure

T, K	Cp, kJ/(kg·K)	T, K	Cp, kJ/(kg·K)
175,49	2,2118	258,15	2,3369
178,15	2,2108	263,15	2,3560
183,15	2,2096	268,15	2,3766
188,15	2,2096	273,15	2,3986
193,15	2,2107	278,15	2,4221
198,15	2,2130	283,15	2,4471
203,15	2,2164	288,15	2,4737
208,15	2,2210	293,15	2,5018
213,15	2,2267	298,15	2,5315
218,15	2,2338	303,15	2,5629
223,15	2,2421	308,15	2,5958
228,15	2,2516	313,15	2,6304
233,15	2,2625	318,15	2,6667
238,15	2,2746	323,15	2,7047
243,15	2,2881	328,15	2,7443
248,15	2,3030	333,15	2,7858
253,15	2,3193	337,70	2,8250

TABLE 3. Isobaric Specific Heat (kJ/(kg·K)) of Liquid Alcohols at Atmospheric Pressure

T, K	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	C ₁₆	C ₁₇	C ₁₈
293,15	2,271	—	—	—	—	—	—	—
303,15	2,361	2,358	—	—	—	—	—	—
313,15	2,452	2,443	2,433	2,407	—	—	—	—
323,15	2,542	2,528	2,515	2,495	2,484	—	—	—
333,15	2,627	2,610	2,596	2,579	2,565	2,550	2,533	—
343,15	2,708	2,688	2,672	2,656	2,640	2,629	2,622	2,607
353,15	2,783	2,761	2,742	2,726	2,708	2,700	2,696	2,686
363,15	2,851	2,827	2,806	2,788	2,769	2,761	2,757	2,750
373,15	2,911	2,885	2,862	2,843	2,823	2,814	2,807	2,800
383,15	2,963	2,935	2,911	2,889	2,868	2,857	2,848	2,840
393,15	3,007	2,978	2,952	2,928	2,906	2,893	2,879	2,870
403,15	3,044	3,013	2,985	2,960	2,937	2,921	2,904	2,893
413,15	3,074	3,042	3,012	2,985	2,960	2,943	2,923	2,910
423,15	3,097	3,063	3,032	3,004	2,978	2,959	2,938	2,923
433,15	3,114	3,080	3,048	3,018	2,991	2,971	2,948	2,932
443,15	3,127	3,092	3,058	3,029	2,999	2,979	2,956	2,939
453,15	3,136	3,100	3,065	3,036	3,005	2,985	2,963	2,945
463,15	3,142	3,105	3,070	3,040	3,009	2,989	2,968	2,950
473,15	3,147	3,109	3,074	3,044	3,013	2,993	2,973	2,955
483,15	3,151	3,113	3,078	3,048	3,017	2,998	2,979	2,961
493,15	3,156	3,117	3,082	3,052	3,022	3,004	2,986	2,968
503,15	3,163	3,122	3,088	3,059	3,029	3,012	2,994	2,977
513,15	3,173	3,129	3,097	3,068	3,039	3,023	3,005	2,987
523,15	—	3,139	3,108	3,080	3,053	3,037	3,018	3,000
533,15	—	3,152	3,123	3,097	3,070	3,055	3,034	3,016
543,15	—	—	3,141	3,118	3,091	3,075	3,053	3,034
553,15	—	—	3,162	3,143	3,115	3,098	3,075	3,055
563,15	—	—	—	3,174	3,141	3,124	3,101	3,079
573,15	—	—	—	—	3,169	3,151	3,129	3,106
583,15	—	—	—	—	3,196	3,178	3,161	3,137

Finally, the smoothed C_p values of the C_{11} - C_{18} alcohols were described by equations of the form

$$C_p = \sum_{i=0}^n a_i (T/1000)^i, \quad (2)$$

where C_p is the isobaric specific heat, kJ/(kg·K), T is temperature, K.

The coefficients of Eq. (1) were calculated by the method of least squares and are presented in Table 1. Also shown for each alcohol is the temperature range used.

Since methanol, the first member of the series, lies outside the observation range (as does ethanol) so that the literature has no reliable information on C_p , a separate equation of the form of Eq. (1) was constructed for that substance using the most reliable experimental data of [11] and [12], obtained at temperatures of 313-383 and 180-320 K using the coefficients a_i presented in Table 1. The specific heat values of [11], essentially determined in the liquid phase along the saturation curve were recalculated to atmospheric pressure for $T \leq 337.70$ K. The value of the correction was less than 0.1%.

The possible error of the recommended C_p values (Tables 2 and 3) calculated with Eqs. (1) with the coefficients presented in Table 1 for methanol for the temperature range from the fusion point ($T = 175.49$ K [10]) to the boiling point ($T = 337.70$ K) is in the range 0.1-0.3% while the corresponding value for the C_{11} - C_{18} alcohols is approximately 2.5%.

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