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Direct Evaluation of the Bubble Point of Multicomponent Ideal Mixtures

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Abstract

A direct method for the evaluation of the bubble point of multicomponent ideal mixtures is presented. The bubble point is less than the average boiling point by a temperature increment Δt. An equation was derived which gives the value of Δt in terms of the average boiling point $t_{a\omega}$ and the total pressure $\pi_{(1)}$ calculated for a bubble point equal to $t_{a\omega}$. For mixtures containing up to four components, a simple formula was found to give quite satisfactory answers. When the number of components increases up to 10, a correction factor was included leading to values of Δt with maximum error less than 2%.

The bubble point t_B of a multicomponent ideal mixture under a given pressure π is calculated by trial and error whereby a temperature is assumed and the total pressure corresponding to it is calculated. If the assumed temperature is correct, then the calculated pressure is equal to π, otherwise another temperature is assumed, the calculations are repeated, and so on.

One usually starts with the average boiling point $t_{b_{a\omega}}$ defined by

$$t_{b_{av}} = \sum x_i t_{b_i} \tag{1}$$

t_{b_i} is the boiling point of pure component i under the given pressure and x_i is its mole fraction. For simplicity, we denote $t_{b_{av}}$ by t_{av}.

In the case of ideal mixtures, the average boiling point t_{av} is greater than the bubble point which is the true boiling point of the mixture. The difference between the two temperatures is denoted by Δt such that

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$$t_B = t_{av} - \Delta t \tag{2}$$

The purpose of this work is to develop a direct method for the determination of Δt and consequently t_B when the mole fractions of the different components, their Antoine constants, and the total pressure π are known.

This study will be devoted only to the case where the total pressure π is 1 atm. The results of this work can then be easily extended to values of π other than atmospheric.

Starting with t_{av} which is greater than t_B, the corresponding total pressure $\pi_{(1)}$ will also be greater than π. As will be shown later, an approximate value $\Delta t_{(1)}$ for Δt can be derived in terms of t_{av}, $\pi_{(1)}$, and π.

Substituting in Eq. (2) gives

$$t_{B(1)} = t_{av} - \Delta t_{(1)} \tag{3}$$

$t_{B(1)}$ is a better value for t_B than t_{av}. Repeating the same calculations for $t_{B(1)}$ leads to a more accurate value $t_{B(2)}$ and so on. The value of $t_{(r)}$, where r is the number of iterations, approaches t_B as r increases.

The aim here is to find the best equation for $\Delta t_{(r)}$, which reduces the number of iterations to a minimum, say one or two only. To this end we proceed as follows.

We first consider the case of a single component having a vapor pressure P_2 at temperature t_2 and we calculate the incremental decrease in temperature Δt needed to reduce the vapor pressure from P_2 to P_1.

Starting with the Antoine equation, namely

$$\ln P = A - \frac{B}{t + C} \tag{4}$$

P is the vapor pressure in mm Hg, t is temperature in °C, and A, B, and C are constants.

On differentiating Eq. (4), one gets

$$\frac{d \ln P}{dt} = \frac{B}{(t + C)^2} \tag{5}$$

For a moderately small temperature increment, Eq. (5) may be rewritten as

$$\frac{\Delta \ln P}{\Delta t} = \frac{B}{(t + C)^2} \tag{6}$$

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leading to

$$\Delta t = \frac{(t + C)^2}{B} \ln \frac{P_2}{P_1} \tag{7}$$

Equation (7) gives a good estimate of Δt in the case of a single component. The accuracy increases as $P_2 - P_1$ and correspondingly Δt get smaller and smaller. It should, however, give a fairly good estimate of Δt in the case of a multicomponent ideal mixture in which case t is replaced by $t_{b_{av}}$. For ideal mixtures of the paraffin series, the Constants B and C are taken as those of a hypothetical member of the series having a boiling point equal to t_{av}. Their values may be obtained from Table 1 where the constants A, B, and C are tabulated for different members of the paraffin series between C_6 and C_{26}. These constants are to be found in several references in the literature including Reid, Prausnitz, and Sherwood's book on the properties of gases and liquids (*1*). The normal

TABLE 1

Values of the Antoine Constants, the Normal Boiling Point t_{bn}, and $(t_{bn} + C)^2/B$ for Different Members of the Normal Paraffin Hydrocarbon Series

Carbon number	A	B	C	t_{bn} (°C)	$(t_{bn} + C)^2/B$
6	15.8366	2697.55	224.40	68.7	31.85
7	15.8737	2911.32	216.69	98.4	34.10
8	15.9426	3120.29	209.57	125.7	36.02
9	15.9671	3291.45	201.87	150.8	37.79
10	16.0114	3456.80	194.53	174.1	39.31
11	16.0541	3614.07	187.75	195.9	40.73
12	16.1134	3774.56	181.89	216.3	42.01
13	16.1355	3892.91	174.27	235.5	43.13
14	16.1480	4008.52	167.8	253.6	44.30
15	16.1724	4121.51	161.4	270.7	45.30
16	16.1841	4214.91	154.5	286.9	46.22
17	16.1510	4294.55	149.2	302.0	47.40
18	16.1232	4361.79	143.3	316.3	48.43
19	16.1533	4450.44	137.6	329.9	49.11
20	16.4685	4680.46	132.1	343.8	48.39
21	16.2954	4656.98	125.5	356.5	49.89
22	16.3120	4729.51	120.1	368.6	50.50
23	16.3279	4798.13	114.8	380.1	51.05
24	16.3428	4863.06	109.6	391.3	51.59
25	16.3571	4924.77	104.6	401.9	52.09
26	16.3705	4983.48	99.6	412.2	52.56

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boiling point t_{b_n} of different members and at $\pi = 760$ mmHg was calculated using Eq. (4) and is given in the same table. The last column in Table 1 lists values of $(t_{b_n} + C)^2/B$ which is also plotted in Fig. 1 vs t_{b_n}. In the case of a multicomponent mixture, t_{b_n} is replaced by $t_{b_{av}}$ or simply t_{av} as defined by Eq. (1).

As a convenient alternative to interpolation in Table 1, an expression was deduced for $(t_{av} + C)^2/B$ in terms of t_{av} utilizing curve-fitting techniques developed by Said and coworkers (*2*, *3*), leading to

$$\frac{(t_{av} + C)^2}{B} = 32 + \frac{0.076(t_{av} - 70)}{1 + 0.00077(t_{av} - 70)} \tag{8}$$

Equation (8) leads to quite small deviations from the values listed in Table 1 for single components and may be used as a good approximation for a mixture of paraffin hydrocarbons. Therefore, on substituting in Eq. (7), one gets

$$\Delta t_{(1)} = \left(\ln \frac{\pi_{(1)}}{760}\right)\left[32 + \frac{0.076(t_{av} - 70)}{1 + 0.00077(t_{av} - 70)}\right] \tag{9}$$

$\pi_{(1)}$ is the total pressure corresponding to a mixture temperature equal to t_{av}:

$$\pi_{(1)} = \sum x_i P_i \tag{10}$$

P_i is the vapor pressure of component i at t_{av} as calculated from Eq. (4).

$\Delta t_{(1)}$ represents a first approximation of Δt in the case of multicomponent ideal hydrocarbon mixtures. For more accurate values of Δt, other iterations are performed whereby the calculations are repeated using a better value for t_B, namely $t_{av} - \Delta t_{(1)}$, leading to $\pi_{(2)}$ and $\Delta t_{(2)}$ and so on.

In fact, Eq. (9) was found to lead to satisfactory answers for mixtures containing up to four components and $\Delta t_{(1)}$ was quite close to the actual Δt. Hence one iteration only is sufficient in most cases and a direct evaluation of the bubble point is accomplished using Eq. (9). In the rare cases where more accuracy is required, a second iteration leads practically to the exact answer.

For mixtures containing more than four components, a second iteration becomes necessary.

To avoid using a second iteration in the case of multicomponent mixtures containing up to 10 components, Eq. (9) was modified by

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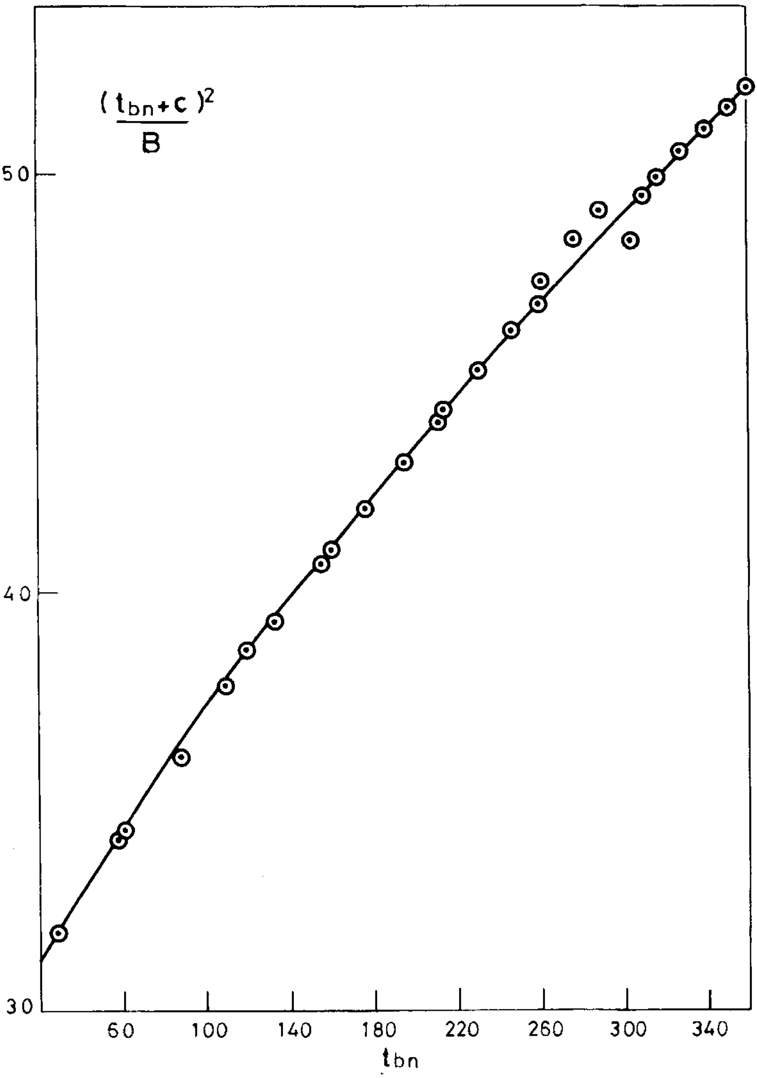

FIG. 1. Plot of $(t_{bn} + C)^2/B$ vs t_{bn}.

multiplying the right-hand side by an empirical correction factor which is a function of both t_{av} and $\pi_{(1)}$, leading to

$$\Delta t_{(1)} = \left(\ln \frac{\pi_{(1)}}{760}\right)\left[32 + \frac{0.076(t_{a\omega} - 70)}{1 + 0.00077(t_{a\omega} - 70)}\right] \times \left[1 + 0.00056(t_{av} + 150) \ln \frac{\pi_{(1)}}{760}\right] \tag{11}$$

Using one iteration only, Eq. (11) leads to quite satisfactory answers for mixtures containing up to 10 components, as can be seen from Table 2.

TABLE 2
Comparing Accuracies of Eqs. (9) and (11) When Utilized in Calculating the Bubble Points of 10 Component Mixtures.

Components	Type 1	Type 2	Type 3	Type 4
C_n	0.19	0.1	0.01	0.01
C_{n+1}	0.17	0.1	0.03	0.03
C_{n+2}	0.15	0.1	0.10	0.05
C_{n+3}	0.13	0.1	0.16	0.07
C_{n+4}	0.11	0.1	0.20	0.09
C_{n+5}	0.09	0.1	0.20	0.11
C_{n+6}	0.07	0.1	0.16	0.13
C_{n+7}	0.05	0.1	0.10	0.15
C_{n+8}	0.03	0.1	0.03	0.17
C_{n+9}	0.01	0.1	0.01	0.19

				Using Eq. (9)		Using Eq. (11)	
n	Type	t_{av}	Δt	$E_{(1)}$ %	$E_{(2)}$ %	$E_{(1)}$ %	$E_{(2)}$ %
6	1	142.3	31.9	−10.1	−0.3	1.2	0.0
6	2	179.0	47.0	−14.9	−0.8	0.8	0.0
6	3	182.9	19.8	−8.2	−0.3	−0.4	0.0
6	4	215.8	33.8	−13.7	−1.0	−1.5	−0.1
11	1	225.2	6.3	−5.2	−0.1	0.8	0.0
11	2	234.5	7.4	−8.0	−0.3	0.7	0.0
11	3	235.0	4.5	−3.6	−0.1	0.5	0.0
11	4	243.8	6.7	−6.3	−0.2	0.5	0.0
16	1	308.8	3.3	−3.1	0.0	0.5	0.0
16	2	315.9	3.8	−4.7	−0.1	0.5	0.0
16	3	316.2	2.3	−2.0	0.0	0.3	0.0
16	4	323.0	3.4	−3.5	−0.1	0.4	0.0

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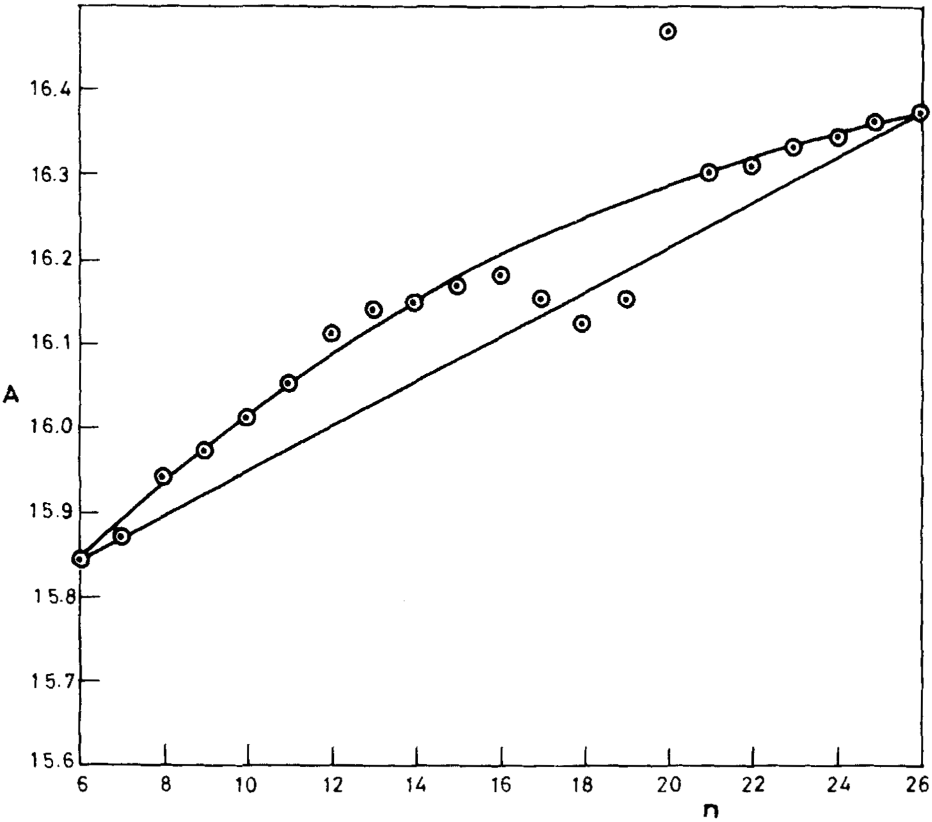

FIG. 2. Plot of Antoine constant A vs n for the hydrocarbon paraffin series.

This table gives the percent error in Δt using Eqs. (9) and (11) for 12 different 10-component mixtures. The mixtures are divided into three groups. Each group has the same 10 components but with different compositions as given by the four types shown at the top of the table. n is the carbon number of the first member of the mixture.

$$E_{(1)}\,\% = \frac{\Delta t_{(1)} - \Delta t}{\Delta t} \times 100$$

$$E_{(2)}\,\% = \frac{\Delta t_{(2)} - \Delta t}{\Delta t} \times 100$$

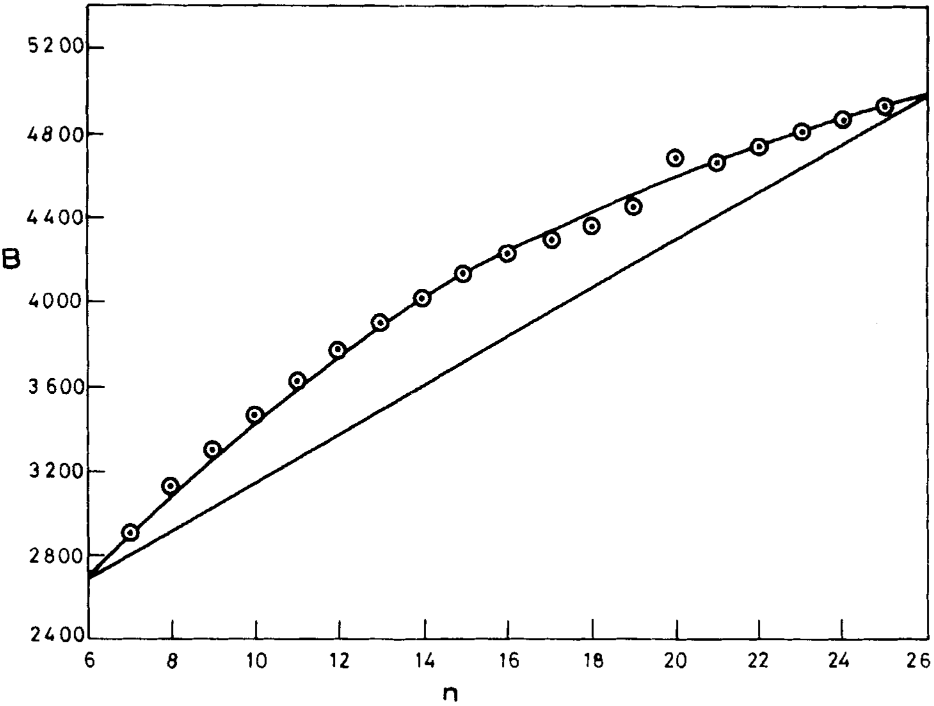

FIG. 3. Plot of Antoine constant B vs n for the hydrocarbon paraffin series.

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where $\Delta t_{(1)}$ and $\Delta t_{(2)}$ are the values of Δt calculated after one iteration (directly) or two iterations, respectively.

A direct evaluation of the bubble point of multicomponent ideal mixtures containing up to 10 components is, therefore, accomplished utilizing Eq. (11). The steps for the direct solution are simply the following:

(1) Calculate t_{av} using Eq. (1)
(2) Calculate P_i for all components at t_{av} using Eq. (4)
(3) Calculate $\pi_{(1)}$ using Eq. (10)
(4) Substitute t_{av} and $\pi_{(1)}$ in Eq. (11) and calculate $\Delta t_{(1)}$
(5) $\Delta t \cong \Delta t_{(1)}$
(6) $t_B = t_{av} - \Delta t$

In the case of mixtures containing up to four components, Eq. (9) may be used instead of Eq. (11).

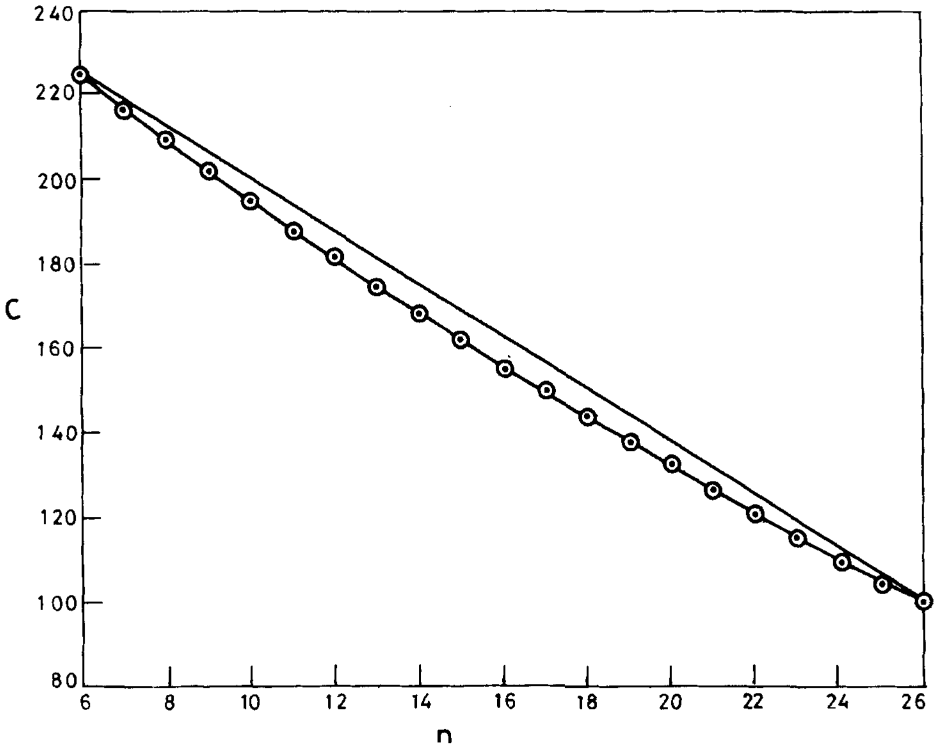

FIG. 4. Plot of Antoine constant C vs n for the hydrocarbon paraffin series.

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To facilitate calculations even further, simple relations were deduced for the Constants A, B, and C in terms of the carbon number n. This was accomplished by plotting the three constants vs n in Figs. 2, 3, and 4, respectively. The best smooth curve going through the different points was plotted, and using curve-fitting techniques the following simple relations were found to fit the constants best:

$$A = 15.84 + 0.056\frac{n-6}{1+0.056(n-6)} \tag{12}$$

$$B = 2680 + \frac{4600(n-6)}{n+14} \tag{13}$$

$$C = 222.4 - \frac{7.8(n-6)}{1+0.0135(n-6)} \tag{14}$$

The normal boiling points of different components calculated using A, B, and C from Eqs. (12), (13), and (14) were found to agree quite well with the experimental boiling points of these components, indicating the usefulness and accuracy of the above equations.

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