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Calculation of Bubble and Dew Points of Ideal Multicomponent Mixtures by Using Statistical Methods. Part I. The Paraffinic Series

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Abstract

Statistical moments are utilized to develop a noniterative method for the calculation of the bubble and dew points of ideal multicomponent mixtures. This approach eliminates the need for Antoine's constants and only requires the mole fraction of each component in the mixture and the normal boiling points. Three homologous series (normal paraffins, olefins, and selected members of the alkylbenzene series) were investigated, and the bubble and dew points calculated by using the statistical method proved to be quite accurate. In Part I of this series the basic equations used to develop this approach are discussed in detail. The computed bubble and dew points are presented for the normal paraffinic series and compared with those obtained from the conventional trial-and-error method. The average temperature difference for bubble point ranges between 0.012 and 0.192°C, giving an average relative error range of 0.008–0.091%. The corresponding ranges for dew point calculations are 0.013–0.672°C and 0.009–0.255%, respectively. The statistical approach can save up to 60% of computer CPU time for 10-component mixtures. In Part II the results for the olefins and the alkylbenzene series will be presented, together with results at pressures other than atmospheric for the three homologous series. Also, the results are compared with experimental values for multicomponent systems whose VLE data are available.

INTRODUCTION

The bubble point (t_B) of a multicomponent ideal mixture under a given pressure (P) is conventionally calculated by assuming a reasonable initial value of temperature. The corresponding total pressure is calculated. The calculated pressure should be equal to the system pressure P, if the assumed temperature is correct. Otherwise, another temperature is assumed and the calculations are repeated until both pressures converge.

Therefore, at the bubble point:

$$\sum_{i=1}^{n} p_i = P \tag{1}$$

where p_i is the partial pressure of Component i
n is the number of components in the mixture

According to Raoult's law for an ideal mixture:

$$p_i = x_i P_i^\circ = y_i P \tag{2}$$

or

$$\sum_{i=1}^{n} x_i (P_i^\circ / P) = \sum_{i=1}^{n} y_i = 1 \tag{3}$$

where x_i is the mole fraction of Component i in the liquid phase
P_i° is the vapor pressure of pure Component i at the temperature under consideration
y_i is the mole fraction of Component i in the vapor phase

Similarly, at the dew point:

$$\sum_{i=1}^{n} y_i (P / P_i^\circ) = \sum_{i=1}^{n} x_i = 1 \tag{4}$$

The vapor pressure of a pure component at any temperature t is obtained from the Antoine equation:

$$\ln P_i^\circ = A - B/(t + C) \tag{5}$$

where P_i° is the vapor pressure, mmHg
t is the temperature, °C
A, B, C are Antoine's constants

Said and Al-Haddad (*1*) utilized the curve-fitting techniques (*2*) to fit the bubble and dew point curves for binary ideal mixtures. The bubble point curve for the system benzene–toluene was fitted at atmospheric pressure quite accurately by the inverse linear function. The relative error was reported to be about 3.8%. The dew point curve for the same system was best fitted by the logarithmic function which yielded a relative error of 7.7%. The curve-fitting techniques were found to be applicable to other hydrocarbons, particularly to the paraffinic series.

Said and coworkers (*3*) derived an equation for direct evaluation of bubble points of multicomponent ideal mixtures, given the mole fraction, boiling point, and Antoine constants for each component in the mixture. They derived an equation which predicts the value of the bubble temperature increment Δt_B. For mixtures containing up to 10 components, the maximum error in the calculated Δt_B was less than 2%.

In the present work, statistical moments are used to develop formulas for the calculation of bubble and dew points of ideal multicomponent mixtures. The developed method eliminates the iteration procedure used in the conventional trial-and-error method. Only the normal boiling points and the mole fractions of the individual components in the mixture are needed for the calculation, eliminating the need for Antoine constants.

THE STATISTICAL APPROACH

The bubble point t_B is less than the average boiling point, t_{av}, of the mixture by a temperature increment, Δt_B:

$$t_B = t_{av} - \Delta t_B \tag{6}$$

Similarly, the dew point t_D is greater than the average boiling point by a temperature increment, Δt_D:

$$t_D = t_{av} + \Delta t_D \tag{7}$$

Statistical moments were used to develop the formulas for Δt_B and Δt_D. The following general formula was utilized to calculate the statistical moments:

$$\mu_r = \sum_{i=1}^{n} x_i(t_{bi} - \mu_1)^r \tag{8}$$

Thus,

$$\text{First moment: } \mu_1 = \sum_{i=1}^{n} x_i t_{bi} \tag{9}$$

$$\text{Second moment: } \mu_2 = \sum_{i=1}^{n} x_i(t_{bi} - \mu_1)^2 \tag{10}$$

$$\text{Third moment: } \mu_3 = \sum_{i=1}^{n} x_i(t_{bi} - u_1)^3 \tag{11}$$

$$\text{Fourth moment: } \mu_4 = \sum_{i=1}^{n} x_i(t_{bi} - \mu_1)^4 \tag{12}$$

The first moment μ_1 is often referred to as the average or the central tendency. This term is used to donate the point about which the data tend to collect. In this case the first moment represents the average boiling point of the mixture.

The second moment μ_2, or the variance, is a fundamental measure of dispersion. It provides a systematic summary of the individual differences and has convenient mathematical properties. However, it is not a convenient practical measure as its units are the square of the units of the variate. Furthermore, many numerical characteristics of distribution are expressed directly in terms of the square root of the variance (*4*). It is therefore preferable to use the square root of the variance or the standard deviation σ to express the dispersion. Standard deviation conveys the same information as the respective variance but in more convenient units (*5*). Here, it can be interpreted as the measure of dispersion of the different boiling points of the components relative to their average boiling point.

Three important indices are calculated from the first four moments:

$$\text{Standard deviation: } \sigma = \pm\sqrt{\mu_2} \tag{13}$$

$$\text{Skewness: } S = \mu_3/\mu_2^{3/2} \tag{14}$$

$$\text{Excess: } E = \mu_4/\mu_2^2 - 3 \tag{15}$$

The skewness, S, is a measure of the asymmetry of the distribution. A symmetrical distribution has a zero skewness, whereas a skewed curve has an unsymmetrical hill shape, with the high part of the curve corresponding to the greatest frequency near one end, rather than being in the middle. Skewed curves take two forms; negatively skewed distribution, which has the longer tail pointing left, and positively skewed distribution, with the longer tail pointing right.

The excess, E, is a measure of the peakness of the distribution relative to the normal distribution. If E is positive, the distribution is more peaked than the corresponding normal distribution and vice versa (*6*).

APPLICATION OF THE STATISTICAL METHOD TO BUBBLE AND DEW POINTS CALCULATIONS FOR THE NORMAL PARAFFINIC SERIES

Starting with mixtures of paraffin hydrocarbons at atmospheric pressure, the conventional trial-and-error procedure was used to calculate the bubble points according to Raoult's law for ideal mixtures.

Successive components between n-C_6H_{14} and n-$C_{17}H_{36}$ were used in these calculations. A list of paraffin hydrocarbons between n-C_6H_{14} and n-$C_{26}H_{54}$, and their normal boiling points within ±0.1°C, is given in Table 1. The calculations were performed on mixtures of 2, 3, 4, 5, and 10 com-

TABLE 1
Normal Boiling Points for Membranes of the Paraffinic Series

Compound	t_{bn} (°C)	Compound	t_{bn} (°C)
n-C_6H_{14}	68.8	n-$C_{17}H_{36}$	302.0
n-C_7H_{16}	98.4	n-$C_{18}H_{38}$	316.3
n-C_8H_{18}	125.6	n-$C_{19}H_{40}$	329.9
n-C_9H_{20}	150.8	n-$C_{20}H_{42}$	343.8
n-$C_{10}H_{22}$	174.1	n-$C_{21}H_{44}$	356.5
n-$C_{11}H_{24}$	195.9	n-$C_{22}H_{46}$	368.6
n-$C_{12}H_{26}$	216.3	n-$C_{23}H_{48}$	380.1
n-$C_{13}H_{28}$	235.4	n-$C_{24}H_{50}$	391.3
n-$C_{14}H_{30}$	253.5	n-$C_{25}H_{52}$	401.9
n-$C_{15}H_{32}$	270.7	n-$C_{26}H_{54}$	412.2
n-$C_{16}H_{34}$	286.9		

TABLE 2
Components and Composition Profiles Tested for the Paraffinic Mixtures

		Composition profiles, mole fractions			
Mixtures	Components	I	II	III	IV
Binary	C_N[a]	0.90	0.50	0.30	0.10
	C_{N+1}	0.10	0.50	0.70	0.90
Tertiary	C_N	0.60	0.333	0.20	0.10
	C_{N+1}	0.30	0.333	0.60	0.30
	C_{N+2}	0.10	0.333	0.20	0.60
Quaternary	C_N	0.40	0.25	0.15	0.10
	C_{N+1}	0.30	0.25	0.35	0.20
	C_{N+2}	0.20	0.25	0.35	0.30
	C_{N+3}	0.10	0.25	0.15	0.40
5-Component	C_N	0.30	0.20	0.10	0.10
	C_{N+1}	0.25	0.20	0.20	0.15
	C_{N+2}	0.20	0.20	0.40	0.20
	C_{N+3}	0.15	0.20	0.20	0.25
	C_{N+4}	0.10	0.20	0.10	0.30
10-Component	C_N	0.19	0.10	0.01	0.01
	C_{N+1}	0.17	0.10	0.03	0.03
	C_{N+2}	0.15	0.10	0.10	0.05
	C_{N+3}	0.13	0.10	0.16	0.07
	C_{N+4}	0.11	0.10	0.20	0.09
	C_{N+5}	0.09	0.10	0.20	0.11
	C_{N+6}	0.07	0.10	0.16	0.13
	C_{N+7}	0.05	0.10	0.10	0.15
	C_{N+8}	0.03	0.10	0.03	0.17
	C_{N+9}	0.01	0.10	0.01	0.19

[a] N takes all values from 6 to 17.

ponents, at four different compositions for each of the above five mixtures as shown in Table 2.

The results show that Δt_B is a function of t_{av}, boiling point span τ, and asymmetry of boiling points around t_{av}. The effect of each of these variables is described below.

A. Effect of Average Boiling Point (t_{av})

In order to find the effect of t_{av}, two mixtures having approximately the same boiling point span τ, of the same asymmetry, i.e., having the same

TABLE 3
Effect of the Average Boiling Point of the Mixture (t_{av}) on the Bubble Point Temperature Increment (Δt_B)

Components of the binary mixtures	t_{av} (°C)	Δt_B (°C)	τ (°C)	$(\Delta t_B)_{\text{corr}}{}^c$ (°C)	K^b
C_7, C_8 (1)	112.01	2.447	27.2	2.447	352.3
C_{18}, C_{20} (2)	330.11	1.702	27.5	1.665	
C_6, C_7 (1)	83.54	3.076	29.6	3.076	448.9
C_{16}, C_{18} (2)	301.69	2.153	29.4	2.182	
C_7, C_9 (1)	124.62	8.519	52.4	8.519	383.4
C_{13},, C_{16} (2)	261.21	6.485	51.5	6.714	
C_6, C_8 (1)	97.18	10.494	56.8	10.494	400.7
C_{11}, C_{14} (2)	224.87	8.589	57.6	8.352	
C_7, C_{10} (1)	136.32	16.601	75.7	16.601	440.8
C_{11}, C_{15} (2)	233.38	13.875	74.8	14.211	
C_8, C_{11} (1)	160.87	13.890	70.3	13.890	416.1
C_{12}, C_{16} (2)	251.63	12.105	70.6	12.001	

[a] $(\Delta t_B)_{corr}$ indicates the corrected Δt_B relative to τ of the first mixture.

[b] $K = (\Delta t_{B(1)} t_{av(1)} - (\Delta t_{B(2)})_{corr} t_{av(2)})/((\Delta t_{B(2)})_{corr} - \Delta t_{B(1)})$.

concentration profile, but with different t_{av}, are compared. Therefore, binary mixtures of composition profile II (uniform component concentrations) are considered as shown in Table 3. Analysis of this table indicates that as t_{av} increases, Δt_B decreases:

$$\Delta t_B \propto 1/(t_{av} + K)$$

It was found that $K = 400$, so that

$$\Delta t_B \propto 1/(t_{av} + 400) \tag{16}$$

B. Effect of the Boiling Point Span τ

To find the effect of the boiling point span, binary mixtures having similar average boiling points, of the same asymmetry, i.e., having the same concentration profile, but differing in the temperature span, are compared as shown in Table 4. The results displayed in this table indicate

TABLE 4
Effect of the Boiling Point Span (τ) on the Bubble Point Temperature Increment (Δt_B)

Components of the binary mixtures	t_{av} (°C)	Δt_B (°C)	τ (°C)	$(\Delta t_B)_{\text{corr}}$[a] (°C)	Z[b]
C_7, C_8 (1)	112.02	2.447	27.2	2.447	1.90
C_6, C_9 (2)	109.78	20.031	82.0	19.94	
C_7, C_9 (1)	124.62	8.519	52.4	8.519	1.81
C_6, C_{10} (2)	121.48	30.289	105.3	30.11	
C_8, C_9 (1)	138.27	1.983	25.2	1.983	1.93
C_7, C_{10} (2)	136.32	16.601	75.7	16.54	
C_9, C_{10} (1)	162.57	1.633	23.3	1.633	1.94
C_8, C_{11} (2)	160.87	13.890	70.3	13.85	
C_9, C_{11} (1)	173.48	5.845	45.1	5.845	1.87
C_8, C_{12} (2)	171.07	21.732	90.7	21.64	
C_{10}, C_{11} (1)	185.18	1.363	21.8	1.363	1.95
C_9, C_{12} (2)	183.68	11.731	65.5	11.69	
C_{11}, C_{12} (1)	206.28	1.151	20.4	1.151	1.96
C_{10}, C_{13} (2)	204.95	9.996	61.3	9.97	
C_{12}, C_{13} (1)	226.06	0.982	19.1	0.982	1.96
C_{11}, C_{14} (2)	224.87	8.589	57.6	0.846	

[a] $(\Delta t_B)_{corr}$ indicates the corrected Δt_B relative to t_{av} of the first mixture.
[b] $Z = (\ln \Delta t_{B(2)})_{corr} - \ln \Delta t_{B(1)})/(\ln \tau_{(2)} - \ln \tau_{(1)})$.

that Δt_B is approximately proportional to the square of the boiling point span of the components in the mixture. This leads to the conclusion that Δt_B is proportional to the variance which is the second moment (as was previously defined in Eq. 10).

$$\Delta t_B \propto \tau^Z$$

where $Z = 2$, so that

$$\Delta t_B \propto \tau^2 \tag{17}$$

i.e.,

$$\Delta t_B \propto \mu_2 \tag{18}$$

C. Effect of the Asymmetry

For a mixture having 90% C_6 and 10% C_7, the average boiling point t_{av} = 71.66°C and Δt_B = 0.939°C, while for a mixture of 10% C_6 and 90% C_7, t_{av} = 95.41°C and Δt_B = 1.345°C. Δt_B for the second mixture is approximately one and a half times Δt_B for the first one, although both mixtures have the same temperature span and consequently the same second moment. Also, the effect of the average boiling points of the two mixtures should have been to decrease Δt_B for the first mixture below Δt_B for the second mixture by a factor of about 5% according to Part A in our analysis. Instead, there was an increase by a factor of 50%. Thus, it was deduced that the only explanation would be due to some parameter which varies drastically for the two mixtures. The only such parameter is the third moment, which is a measure of the asymmetry. It is a large positive quantity for one mixture and a large negative quantity for the other mixture. These two quantities have the same numerical values. The variation of Δt_B with the third moment was found empirically after several trials.

On the basis of the above analysis, the following formula was deduced in terms of the first three moments:

$$\Delta t_B = B \exp(-BS/1.8\sigma) \tag{19}$$

where

$$B = 6.8\mu_2/(\mu_1 + 400) \tag{20}$$

Equation (19) gave satisfactory results for mixtures containing up to four components. In order to extend its application to mixtures containing up to 10 components, it was found necessary to multiply the right-hand side by a correction factor incorporating the fourth moment in the form of the excess (*E*) as shown in the following equation:

$$\Delta t_B = \alpha_1 B \exp(-BS/1.8\sigma) \tag{21}$$

where

$$\alpha_1 = 1 + 0.002BE$$

In the case of the dew point calculations, the following equation was found to give reasonably accurate results:

$$\Delta t_D = D \exp(DS/1.5\sigma) \tag{22}$$

$$\text{where } D = 7.8\mu_2/(\mu_1 + 400) \tag{23}$$

Equation (22) is modified by multiplying the right-hand side by an empirical correction factor incorporating the excess (*E*):

$$\Delta t_D = \alpha_2 D \exp(DS/1.5\sigma) \tag{24}$$

where

$$\alpha_2 = 1 + 0.004(DE + 0.0005\sigma^2)$$

RESULTS AND DISCUSSION

A large number of computer runs were performed to evaluate the developed algorithm using the statistical approach. The computed bubble and dew points for the different paraffinic mixtures using the statistical approach were compared to the corresponding values calculated by the conventional iterative algorithm. The results are shown in Tables 5–9 for binary, tertiary, quaternary, 5-components, and 10-components paraffinic mixtures, respectively. Each table displays the components comprising the mixture; the four composition profiles; the average boiling temperature, t_{av}; the bubble and dew points computed using both statistical and conventional methods; and the relative errors. The temperature increments Δt_B and Δt_D are also shown for convenience.

TABLE 5
Comparison between Conventional and Statistical Methods for Binary Mixtures

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	$E_B{}^a$	E_D^b
C_6, C_7	I	71.674	70.739	73.402	0.955	70.719	1.748	73.422	−0.028	+0.027
	II	83.541	80.480	86.933	3.056	80.485	3.450	86.991	−0.006	+0.067
	III	89.475	86.654	91.985	2.796	86.679	2.560	92.035	−0.029	+0.054
	IV	95.408	94.070	96.373	1.318	94.090	0.997	96.405	−0.021	+0.033
C_9, C_{10}	I	153.099	152.583	153.943	0.532	152.567	0.833	153.932	−0.010	−0.007
	II	162.421	160.819	164.287	1.631	160.790	1.855	164.276	−0.018	−0.007
	III	167.082	165.653	168.511	1.450	165.632	1.429	168.511	−0.013	0.000
	IV	171.744	171.091	172.308	0.662	171.082	0.571	172.315	−0.005	+0.004
C_{12}, C_{13}	I	218.182	217.860	218.677	0.332	217.850	0.478	218.660	−0.005	−0.008
	II	225.841	224.870	227.005	0.992	224.849	1.132	226.973	−0.009	−0.015
	III	229.671	228.819	230.581	0.869	228.802	0.891	230.562	−0.007	−0.008
	IV	233.501	233.119	233.867	0.390	233.111	0.361	233.862	−0.003	−0.002
C_{15}, C_{16}	I	272.281	272.064	272.599	0.221	272.060	0.303	272.584	−0.002	−0.006
	II	278.741	278.099	279.516	0.652	278.089	0.745	279.486	−0.004	−0.010
	III	281.971	281.413	282.586	0.565	281.406	0.595	282.566	−0.003	−0.007
	IV	285.201	284.953	285.451	0.251	284.950	0.244	285.445	−0.001	−0.002
C_{17}, C_{18}	I	303.449	303.280	303.676	0.168	303.281	0.223	303.672	0.000	−0.001
	II	309.172	308.675	309.739	0.490	308.682	0.560	309.732	−0.002	−0.002
	III	312.033	311.603	312.487	0.423	311.610	0.451	312.484	−0.002	0.000
	IV	314.895	314.705	315.081	0.186	314.709	0.186	315.081	−0.001	0.000

[a] $\%\ E_B = [(\text{statistical } t_B - \text{conventional } t_B)/\text{conventional } t_B] \times 100.$

[b] $\%\ E_D = [(\text{statistical } t_D - \text{conventional } t_D)/\text{conventional } t_D] \times 100.$

TABLE 6
Comparison between Conventional and Statistical Methods for Tertiary Mixtures

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
C_6, C_7, C_8	I	83.298	78.807	90.329	4.564	78.734	7.274	90.572	−0.090	+0.269
	II	97.563	90.315	105.331	7.283	90.280	7.943	105.506	−0.039	+0.166
	III	97.889	93.382	102.776	4.481	93.408	4.917	102.806	+0.028	+0.029
	IV	111.750	106.278	116.052	5.456	106.294	4.407	116.157	+0.015	+0.090
C_9, C_{10}, C_{11}	I	162.271	159.772	165.976	2.565	159.708	3.695	165.966	−0.040	−0.006
	II	173.572	169.648	178.038	3.993	169.579	4.459	178.031	−0.041	−0.003
	III	173.774	171.379	176.518	2.429	171.345	2.720	176.494	−0.020	−0.014
	IV	184.826	181.981	187.407	2.881	181.945	2.597	187.423	−0.020	+0.009
C_{12}, C_{13}, C_{14}	I	225.735	224.167	227.976	1.603	224.132	2.184	227.919	−0.016	−0.025
	II	235.058	232.631	237.893	2.464	232.594	2.779	237.837	−0.016	−0.024
	III	235.203	233.729	236.926	1.491	233.712	1.684	236.887	−0.007	−0.016
	IV	244.350	242.623	246.035	1.741	242.609	1.669	246.019	−0.006	−0.007
C_{15}, C_{16}, C_{17}	I	278.646	277.586	280.083	1.068	277.578	1.287	280.045	−0.003	−0.014
	II	286.497	284.871	288.364	1.619	284.878	1.399	288.332	−0.003	−0.011
	III	286.626	285.643	287.752	0.978	285.648	1.835	287.734	−0.002	−0.006
	IV	294.322	293.174	295.447	1.126	293.196	1.108	295.445	−0.008	0.000
C_{17}, C_{18}, C_{19}	I	309.097	308.286	310.173	0.813	308.284	1.044	310.141	0.000	−0.010
	II	316.073	314.854	317.517	1.227	314.846	1.395	317.468	−0.003	−0.010
	III	316.176	315.438	317.046	0.740	315.436	0.841	317.017	0.000	−0.009
	IV	323.030	322.189	323.921	0.849	322.181	0.864	323.894	−0.002	−0.006

TABLE 7
Comparison between Conventional and Statistical Methods for Quaternary Mixtures

Mixture	Composition profile	t_{av} (°C)	Conventional method (°C)		Statistical method (°C)				Relative error (%)	
			t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
C_6, C_7, C_8, C_9	I	97.194	87.997	109.941	9.328	87.866	13.392	110.586	−0.149	+0.587
	II	110.865	98.686	123.389	12.279	98.586	12.849	123.714	−0.101	+0.263
	III	111.316	102.765	120.262	8.549	102.767	9.090	120.406	+0.002	+0.120
	IV	124.536	113.926	133.035	10.642	113.894	8.699	133.235	−0.028	+0.150
C_8, C_9, C_{10}, C_{11}	I	149.877	143.662	158.449	6.338	143.539	8.720	158.597	−0.086	+0.093
	II	161.583	153.465	170.387	8.228	153.355	8.879	170.462	−0.072	+0.044
	III	161.918	156.294	168.103	5.681	156.237	6.192	168.110	−0.036	+0.004
	IV	173.288	166.394	179.392	6.969	166.319	6.166	179.454	−0.045	−0.035
C_{10}, C_{11}, C_{12}, C_{13}	I	195.188	190.747	201.285	4.537	190.651	6.054	201.242	−0.050	−0.021
	II	205.409	199.667	211.877	5.836	199.573	6.408	211.817	−0.047	−0.028
	III	205.674	201.719	210.173	4.012	201.662	4.435	210.109	−0.028	−0.031
	IV	215.629	210.830	220.192	4.869	210.760	4.537	220.166	−0.033	−0.012
C_{12}, C_{13}, C_{14}, C_{15}	I	234.898	231.587	239.397	3.374	231.524	4.407	239.305	−0.027	−0.038
	II	243.962	239.695	248.855	4.319	239.643	4.802	248.764	−0.022	−0.037
	III	244.160	241.231	247.540	2.960	241.200	3.307	247.467	−0.013	−0.030
	IV	253.026	249.484	256.530	3.574	249.452	3.458	256.484	−0.013	−0.018
C_{16}, C_{17}, C_{18}, C_{19}	I	301.585	299.605	304.089	1.954	299.631	2.461	304.046	−0.009	−0.014
	II	308.761	306.259	311.590	2.468	306.293	2.773	311.534	+0.011	−0.018
	III	308.925	307.213	310.862	1.686	307.239	1.898	310.823	−0.009	−0.012
	IV	315.936	313.906	318.012	2.007	313.929	2.036	317.972	−0.007	−0.013

TABLE 8
Comparison between Conventional and Statistical Methods for 5-Component Mixtures

Mixture	Composition profile	t_{av} (°C)	Conventional method (°C)		Statistical method (°C)				Relative error (%)	
			t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
C_6, C_7, C_8, C_9, C_{10}	I	110.351	95.779	129.048	14.774	95.577	19.758	130.109	−0.210	+0.822
	II	123.507	105.945	140.887	17.752	105.755	17.735	141.242	−0.179	+0.231
	III	124.351	113.190	135.653	11.132	113.219	11.448	135.799	−0.026	+0.108
	IV	136.663	120.065	149.767	16.761	119.902	13.335	149.998	−0.136	+0.154
C_8, C_9, C_{10}, C_{11}, C_{12}	I	161.198	151.198	174.26	10.185	151.013	13.367	174.565	−0.122	+0.175
	II	172.519	160.609	185.055	12.077	160.442	12.626	185.145	−0.104	+0.049
	III	173.147	165.746	181.102	7.461	165.686	7.946	181.093	−0.036	−0.005
	IV	183.841	172.824	193.455	11.159	172.682	9.686	193.527	−0.082	+0.037
C_{11}, C_{12}, C_{13}, C_{14}, C_{15}	I	225.004	218.772	233.230	6.351	218.653	8.143	233.147	−0.054	−0.036
	II	234.345	227.002	242.526	7.445	226.900	8.072	242.417	−0.045	−0.045
	III	234.774	230.283	239.852	4.546	230.228	4.981	239.755	−0.024	−0.040
	IV	243.685	237.007	250.093	6.755	236.930	6.346	250.031	−0.045	−0.025
C_{14}, C_{15}, C_{16}, C_{17}, C_{18}	I	278.014	273.823	283.369	4.216	273.798	5.278	283.292	−0.009	−0.027
	II	285.865	280.970	291.303	4.886	280.979	5.374	291.239	−0.003	−0.021
	III	286.245	283.269	289.573	2.968	283.277	3.282	289.527	+0.003	−0.016
	IV	293.715	289.313	298.023	4.366	289.349	4.287	298.002	+0.012	−0.007
C_{16}, C_{17}, C_{18}, C_{19}, C_{20}	I	308.676	305.439	313.056	2.269	305.407	4.084	312.760	−0.010	−0.095
	II	315.767	312.034	320.385	3.806	311.961	4.259	320.026	−0.023	−0.112
	III	315.971	313.711	318.766	2.292	313.679	2.579	318.550	−0.010	−0.067
	IV	322.857	319.562	326.636	3.412	319.445	3.460	326.317	−0.037	−0.098

TABLE 9
Comparison between Conventional and Statistical Methods for 10-Component Mixtures

			Conventional method (°C)		Statistical method (°C)				Relative error (%)	
Mixture	Composition profile	t_{av} (°C)	t_B	t_D	Δt_B	t_B	Δt_D	t_D	E_B	E_D
C_6, C_7, C_8,	I	142.218	110.530	184.152	31.935	110.283	45.147	187.365	−0.223	+1.745
C_9, C_{10}, C_{11},	II	178.926	132.218	218.352	47.307	131.619	36.484	215.410	−0.453	−1.35
C_{12}, C_{13}, C_{14}	III	182.769	163.135	201.207	19.569	163.200	18.564	201.333	−0.040	0.062
C_{15},	IV	215.634	182.190	236.468	34.332	181.302	21.433	237.064	−0.487	0.252
C_8, C_9, C_{10}, C_{11},	I	209.957	190.276	237.065	20.022	189.935	27.970	237.927	−0.179	0.364
C_{12}, C_{13}, C_{14},	II	240.173	211.194	267.343	29.265	210.908	26.318	266.491	−0.135	−0.319
C_{15}, C_{16}, C_{17}	III	242.915	231.182	255.007	11.803	231.112	11.979	254.894	−0.030	−0.044
	IV	270.389	250.439	284.909	20.234	250.155	14.786	285.175	−0.113	+0.093
C_{12}, C_{13}, C_{14}, C_{15},	I	265.570	252.356	284.011	13.377	252.193	18.212	283.782	−0.065	−0.081
C_{16}, C_{17}, C_{18},	II	291.116	271.733	311.038	19.443	271.673	19.001	310.117	−0.022	−0.296
C_{19}, C_{20}, C_{21},	III	293.127	285.432	301.465	7.675	285.452	8.071	301.198	0.007	−0.089
	IV	216.663	203.672	227.629	13.114	203.549	10.678	227.341	−0.105	−0.127
C_{15}, C_{16}, C_{17}, C_{18},	I	312.536	303.280	325.757	9.368	303.168	12.579	325.115	−0.037	−0.197
C_{19}, C_{20}, C_{21},	II	334.592	321.038	349.430	13.632	320.960	13.988	348.580	−0.024	−0.243
C_{22}, C_{23}, C_{24},	III	336.069	330.807	342.344	5.403	330.666	5.855	341.924	−0.043	−0.123
	IV	356.069	347.091	364.330	9.123	346.946	7.932	364.001	−0.042	−0.09
C_{17}, C_{18}, C_{19}, C_{20},	I	340.067	332.653	350.875	7.638	332.429	10.090	350.967	−0.067	+0.027
C_{21}, C_{22}, C_{23},	II	360.251	349.364	372.615	11.062	349.189	11.541	371.792	−0.050	−0.221
C_{24}, C_{25}, C_{26},	III	361.636	357.317	366.708	4.371	357.265	4.745	366.381	−0.015	−0.089
	IV	380.434	373.172	387.344	7.323	373.11	6.569	387.003	−0.017	−0.088

As can be seen from Tables 5-9, the maximum relative error was consistently obtained, within each group, for mixtures containing the lighter components hexane and heptane. For instance, the maximum difference recorded in bubble point calculations ranges between 0.02°C (0.028% relative error) for binary mixtures and 0.60°C (0.453%) for 10-component mixtures. The corresponding differences recorded in dew point calculations were 0.06°C (0.067%) and 3.21°C (1.745%) for binary and 10-component mixtures, respectively. Since the denominator, in the formula defining the relative error, increases as the number of carbon atoms increases, the maximum relative error decreases considerably for both bubble and dew point calculations. For instance, for mixtures containing n-C_{16} and above, the maximum differences recorded in bubble point calculations were between 0.01°C (0.004%) for binary mixtures and 0.224°C (0.067%) for 10-component mixtures. The corresponding differences for t_D were 0.03°C (0.01%) and 0.85°C (0.243%) for binary and 10-component mixtures, respectively.

The results from all computer runs were averaged within each group for ease of comparison. The number of tested mixtures was 48 for each of the binary, tertiary, and 10-components systems, and 44 for each of the quaternary and 5-components systems. Average values of the temperature differences, relative errors, and computer CPU time consumption were calculated and plotted as shown in Figs. 1-3, respectively.

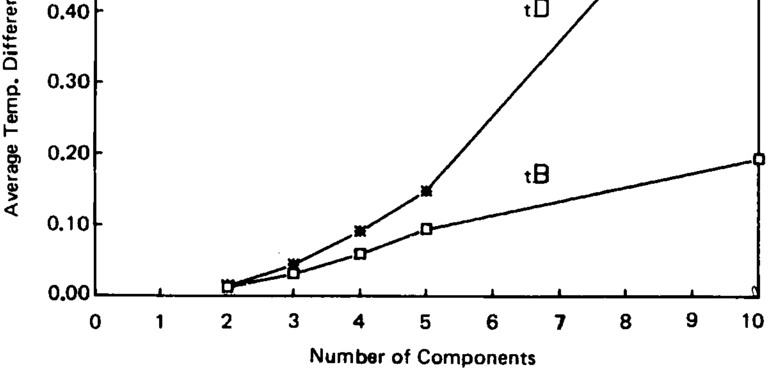

FIG. 1. Average temperature difference as a function of the number of components.

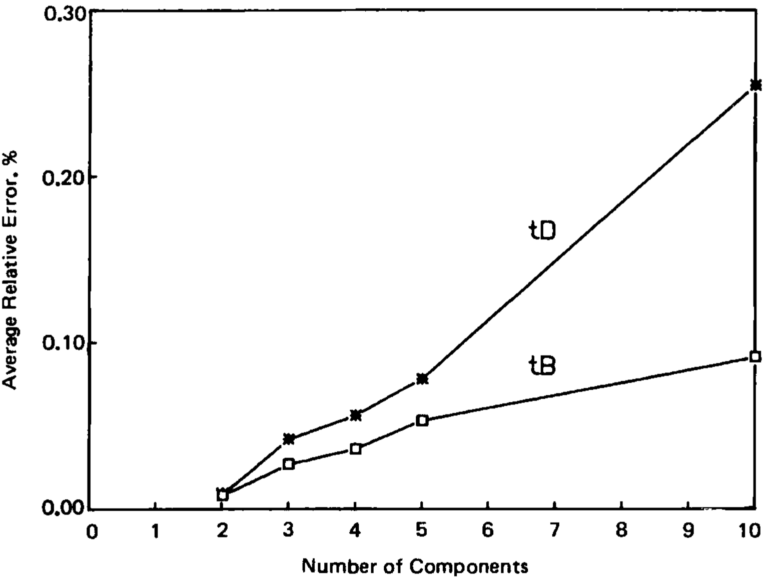

FIG. 2. Average relative error as a function of the number of components.

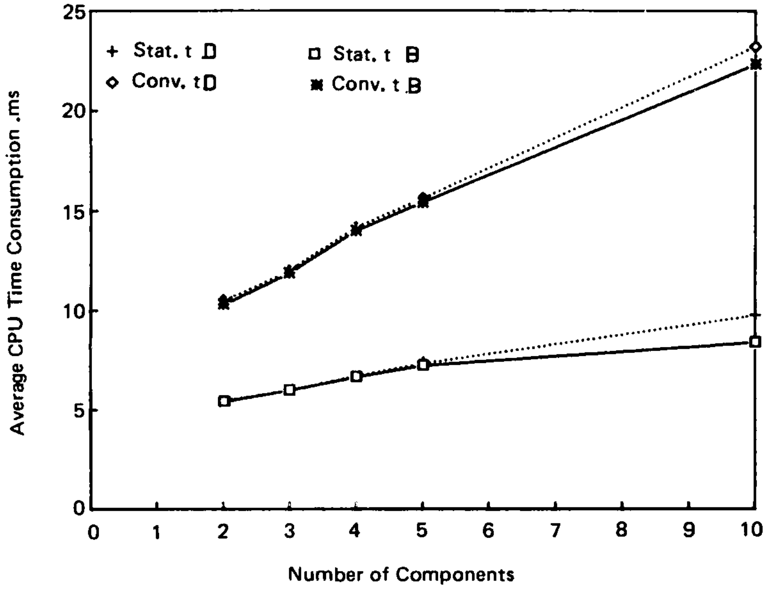

FIG. 3. Average computer CPU time as a function of the number of components

For the 5 multicomponent groups investigated, the average temperature differences for the bubble point range between 0.012 and 0.192°C, resulting in an average relative error range of 0.008–0.091%. The corresponding ranges for the dew points were 0.013–0.672°C for the average temperature differences and 0.009–0.255% for the average relative errors.

Figure 3 clearly shows that up to 5 components, there is practically no difference in the average computer CPU time consumed in calculating the bubble and dew points. The difference increases, as expected, with an increase in the number of components. Using a UNISYS model 1172 mainframe, about 60% of the computer CPU time can be saved by using the statistical approach. This saving decreases as the number of components in the mixture decreases. Thus, for a binary mixture, the saving in CPU time was about 48%.

In conclusion, the results obtained by using Eqs. (21) and (24) indicate that the calculated bubble and dew points using the statistical approach proved to be quite accurate and more economic to simulate. In Part II of this work, the results for the olefins and the alkylbenzene series will be presented, together with results at pressures other than atmospheric for the three homologous series. Also, the calculated results are compared with experimental values for multicomponent systems whose VLE data are available.

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