The Critical Temperatures of Multicomponent Hydrocarbon Systems

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The critical temperature of any multicomponent hydrocarbon system may be established solely from the normal boiling points of the pure constituents. Such mixtures may include normal paraffins, isoparaffins, olefins, acetylenes, naphthenes, and aromatics and may contain an unlimited number of components.

An expression has been developed for the prediction of the critical temperatures of mixtures and has been tested on fifty-five hydrocarbon systems containing from two to five components. For 208 binary mixtures the deviations from reported values were calculated, and the maximum deviations resulting from each system were averaged for the forty-one binary systems to produce an average maximum deviation of 0.91% based on degrees absolute. For twenty-eight multicomponent mixtures reported for nine ternary, two quaternary, and three quinary systems the average deviation was 1.03%.

This method presents a simple and accurate means of establishing the critical temperature of any multicomponent hydrocarbon mixture as long as the ratio of the normal boiling points of the heaviest and lightest components present in the mixture does not exceed the prescribed limits.

The subject concerned with the critical state of multicomponent mixtures is important in establishing the limiting case of vapor-liquid phase behavior. In reservoir engineering the critical temperatures of natural gas mixtures within the formation are important in establishing the possibility of liquefaction in the underground structure due to retrograde condensation. In addition modern trends indicate that the application of the theorem of corresponding states for mixtures is more amenable to the use of the actual critical state as a basis rather than the pseudocritical state. Thus a knowledge of the critical state of multicomponent mixtures is of considerable importance in many areas of chemical engineering.

From a consideration of the existing methods of predicting the critical temperatures of mixtures (*7, 9, 10, 13, 23, 40*) no method was found which could establish in a simple manner the critical temperature of hydrocarbon mixtures containing an unlimited number of components of all types. Therefore a comprehensive analysis of presently available critical-temperature data was attempted in order to develop a direct and accurate method for the establishment of this value from a minimum number of properties of the pure components.

To this end the screening of several expressions that contained the pure component critical temperatures, the composition of the mixture, and necessary constants, and which also reduced to the pure component critical temperatures in the limiting case of the compositions corresponding to the pure components, showed the following expression to be acceptable:

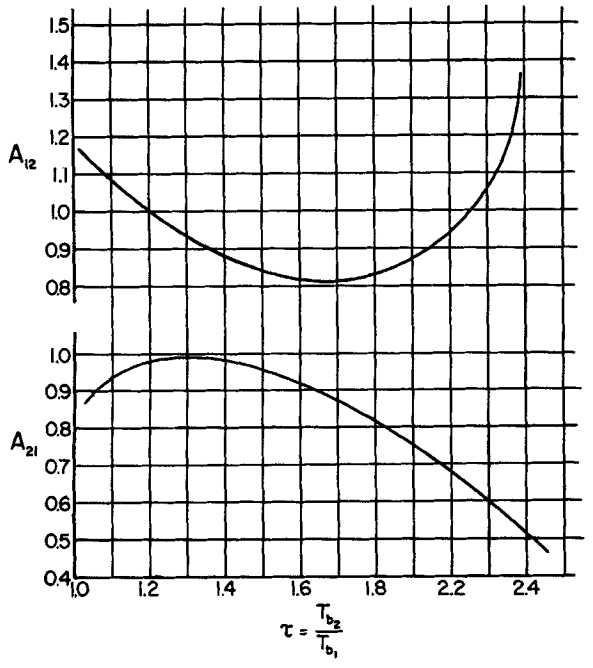

Fig. 1. Relationships between binary temperature coefficients and normal boiling-point ratio (nonmethane systems).

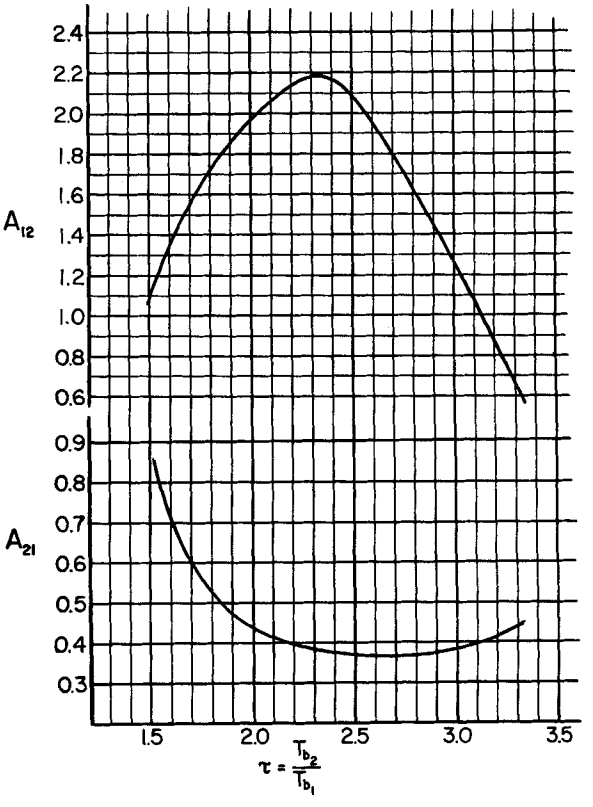

Fig. 2. Relationships between binary temperature coefficients and normal boiling-point ratio (methane systems).

$$T_{cm} = \sum_{i=1}^{n} \frac{T_{ci}}{1 + \frac{1}{x_i} \sum_{\substack{j=1 \\ j \neq i}}^{n} A_{ij} x_j} \quad (1)$$

For a binary system this expression reduces to the following:

$$T_{cm} = \frac{T_{c1}}{1 + \frac{x_2}{x_1} A_{12}} + \frac{T_{c2}}{1 + \frac{x_1}{x_2} A_{21}} \quad (2)$$

For a ternary system this expression reduces to

$$T_{cm} = \frac{T_{c1}}{1 + \frac{x_2}{x_1} A_{12} + \frac{x_3}{x_1} A_{13}} + \frac{T_{c2}}{1 + \frac{x_1}{x_2} A_{21} + \frac{x_3}{x_2} A_{23}} + \frac{T_{c3}}{1 + \frac{x_1}{x_3} A_{31} + \frac{x_2}{x_3} A_{32}} \quad (3)$$

For a four-component system twelve coefficients appear, for a five-component system twenty coefficients appear, for an n-component system $n(n-1)$ coefficients appear. Upon examination of the expanded binary and ternary expressions it is clear that a pure component critical temperature is obtained in the limiting case when the composition corresponds to a pure substance. It is also obvious that the addition of a third component to a binary mixture should not affect the set of the binary temperature coefficients (A_{12}, A_{21} or A_{13}, A_{31} or A_{23}, A_{32} etc.). Thus for a three-component system three sets of binary coefficients are required, each set applying to one of the three binary systems comprising the ternary. In a similar manner for a four-component system six sets of binary coefficients are required, each set applying to one of the six binary systems comprising the quaternary. For an n-component system $n(n-1)/2$ sets of binary coefficients are needed.

A preliminary investigation of data for several normal paraffin binary and ternary systems indicated the feasibility of using Equation (1) to predict critical temperatures. The essential point that this preliminary study verified was that the sets of binary coefficients obtained from binary critical-temperature data could be applied successfully to multicomponent systems.

BINARY SYSTEMS

An extensive study was made of all critical temperature data appearing in the literature for binary hydrocarbon systems. The forty-one systems considered included components from the paraffins, olefins, acetylenes, naphthenes, and aromatics. A list of the systems considered appears in Table 1. For each binary system a set of coefficients A_{12}, A_{21} was determined by substituting critical temperature-composition values in Equation (2). For the forty-one systems the 208 reported compositions were utilized, averaging about five compositions for each system. For several systems a large number of allowable sets of coefficients were obtained; for several others only one set of coefficients resulted.

The general trend in the values of the binary coefficients indicated that they were related to the normal boiling-point range of the two components involved. It also seemed possible that the normal boiling point could handle adequately all types of hydrocarbons. Therefore a correlation was attempted between the set of binary constants, A_{12}, A_{21}, and $\tau = T_{b2}/T_{b1}$, the normal boiling-point ratio of the pure components. The components were numbered so that τ was always greater than 1.0. For twenty-five nonmethane, nonaromatics binary systems containing paraffins, olefins, acetylenes, and naphthenes it was found that A_{12}, A_{21} could be determined solely from the parameter τ. This relationship appears as

TABLE 1. SYSTEMS INVESTIGATED AND EXPECTED CRITICAL TEMPERATURE DEVIATIONS

Binary systems	Max. dev., %
Methane-ethane (*4*)	0.26
Methane-propane (*32*)	0.58
Methane-*n*-butane (*37*)	0.74
Methane-*n*-pentane (*39*)	1.57
Methane-*n*-heptane (*33*)	2.98
Ethane-propane (*24*)	0.69
Ethane-*n*-butane (*18*)	0.34
Ethane-*n*-pentane (*35*)	0.34
Ethane-*n*-heptane (*17*)	0.64
Propane-*n*-butane (*27*)	1.24
Propane-*n*-pentane (*38*)	0.25
n-Butane-*n*-pentane (*10*)	0.37
n-Butane-*n*-heptane (*19*)	0.26
n-Butane-*n*-decane (*31*)	1.05
n-Pentane-*n*-hexane (*29*)	0.45
n-Pentane-*n*-heptane (*6*)	0.45
Methane-isobutane (*28*)	1.79
Methane-isopentane (*1*)	0.25
Propane-isopentane (*41*)	0.25
n-Pentane-neopentane (*29*)	0.38
n-Hexane-neopentane (*29*)	0.25

Binary systems	Max. dev., %
Methane-ethylene (*14*)	0.48
Ethane-propylene (*26*)	0.31
Propane-butene-1 (*12*)	0.82
n-Butane-ethylene (*42*)	1.68
n-Heptane-ethylene (*20*)	0.48
Propane-acetylene (*25*)	1.89
Methane-cyclohexane (*34*)	2.72
Ethane-cyclohexane (*21*)	0.82
n-Pentane-cyclohexane (*29*)	1.00
n-Hexane-cyclohexane (*29*)	0.22
Ethane-benzene (*22*)	1.86
Propane-benzene (*11*)	1.62
n-Pentane-benzene (*29*)	1.83
n-Hexane-benzene (*29*)	0.64
n-Pentane-toluene (*29*)	0.80
n-Hexane-toluene (*29*)	1.23
Ethylene-propylene (*16*)	0.38
Propylene-acetylene (*25*)	0.89
Neopentane-cyclohexane (*29*)	0.60
Neopentane-benzene (*29*)	1.73

Ternary systems	Number of mixtures	Dev., %
Methane-ethane-propane (*30*)	3	1.03
Methane-ethane-*n*-butane (*5*)	5	0.57
Methane-ethane-*n*-pentane (*3*)	3	1.42
Methane-propane-*n*-butane (*36*)	4	1.52
Methane-propane-*n*-pentane (*7*)	2	0.48
Methane-ethylene-isobutane (*2*)	2	1.10
Ethane-propane-*n*-pentane (*10*)	1	0.56
Propane-*n*-butane-*n*-pentane (*10*)	1	0.39
n-Butane-*n*-pentane-*n*-hexane (*10*)	1	0.74
Quaternary systems		
Ethane-propane-*n*-butane-*n*-pentane (*10*)	1	0.41
Propane-*n*-butane-*n*-pentane-*n*-hexane (*10*)	1	0.27
Quinary systems		
Methane-ethane-propane-*n*-butane-*n*-pentane (*10, 15*)	2	1.68
Methane-ethane-propane-*n*-pentane-*n*-hexane (*15*)	1	3.22
Ethane-propane-*n*-butane-*n*-pentane-*n*-hexane (*10*)	1	0.58

Figure 1. It should be noted that τ ranges from 1.0 to 2.2 for those systems studied. For the ethylene—*n*-heptane system $\tau = 2.19$.

A separate relationship was developed for the nine available methane systems. Again it was found that A_{12}, A_{21} could be determined solely from τ. This relationship appears as Figure 2. It should be noted that τ ranges from 1.5 to 3.3 for those systems investigated. For the methane-ethylene system $\tau = 1.52$, and for methane—*n*-heptane $\tau = 3.30$. An exception to this behavior is the methane—*n*-butane system for which the values $A_{12} = 0.86$ and $A_{21} = 0.60$ should be used.

For the seven systems considered which contained an aromatic hydrocarbon as one component A_{12}, A_{21} values obtained from Figure 1 can be used, provided the following adjustment is made in the critical temperature of the pure aromatic:

T_c^* (°R.) = T_c (°R.) − 15
for mole fraction aromatic > 0.60

and

T_c^* (°R.) = T_c (°R.) − 40
for mole fraction aromatic < 0.60

For example for benzene $T_c^* = 1{,}010 - 15 = 995$°R. and $T_c^* = 1{,}010 - 40 = 970$°R.

For the total of forty-one binary systems considered the deviations of critical temperatures obtained with Figures 1 and 2 from reported values were calculated for 208 compositions. The maximum deviation for each system is given in Table 1. For nonaromatic systems the average of the maximum deviation is 0.79%, based on degrees absolute. For the aromatic systems the average of the maximum deviations is 1.39%.

MULTICOMPONENT SYSTEMS

The significance of Equation (1) lies in the fact not only that it may be used to predict accurately the critical temperatures of binary systems, but also that the binary coefficients may be utilized for the establishment of the critical temperatures of multicomponent mixtures. For a multicomponent mixture each set of binary coefficients corresponding to each pair of components is obtained from either Figure 1 or Figure 2 and is substituted together with the composition ratios into the appropriate form of Equation (1). The components are numbered in order of increasing normal boiling point. Thus for a ternary system one set of coefficients is evaluated each for $\tau = \frac{T_{b_2}}{T_{b_1}}$, $\tau = \frac{T_{b_3}}{T_{b_1}}$, $\tau = \frac{T_{b_3}}{T_{b_2}}$, where each value of τ is greater than 1.0. For example the set of constants obtained from Figure 1 or Figure 2 corresponding to $\tau = \frac{T_{b_3}}{T_{b_1}}$ is A_{13}, A_{31}, etc. The numbering convention used in developing Figure 1 and Figure 2 may be readily extended in this manner to multicomponent systems. For clarity an example calculation of the critical temperature of a quaternary mixture is included. For multicomponent mixtures containing methane Figure 2 is used only for the sets of binary coefficients corresponding to pairs of components including methane, while Figure 1 produces coefficients for each nonmethane pair of components. The coefficients thus obtained from both figures may then be substituted into the appropriate form of Equation (1). The recommended set of coefficients for the methane-*n*-butane system should also be used for multicomponent calculations.

The quantity of critical temperature data for systems containing three or more components is limited. In order to test the binary constants the critical temperatures of twenty-eight mixtures from fourteen multicomponent systems were calculated. These included nine ternary systems, two quaternary systems, and three quinary systems, which are listed in Table 1, together with the number of compositions considered and the average per cent deviation of the calculated values from the reported values for each system. For the twenty-eight compositions the average deviation is 1.03%, based on degrees absolute. This error is quite acceptable, particularly since much of the multicomponent critical data had to be extrapolated from vapor-liquid equilibrium values. In addition, most of the systems contained methane, which usually causes extensive correlation difficulties.

Example

Establish the critical temperature of a quaternary hydrocarbon mixture having the following composition:

		Mole fraction	T_b, °R.	T_c, °R.
1	Ethane	0.254	331.7	549.5
2	Propane	0.255	416.1	666.0
3	*n*-Butane	0.255	491.6	765.7
4	*n*-Pentane	0.236	556.6	847.1
		1.000		

For this system there exist six binary pairs, each of which determines a set of binary coefficients. These coefficients are obtained from Figure 1 and are listed below together with the τ values.

	τ	Temperature coefficients	
Ethane-propane	1.254	$A_{12} = 0.966$	$A_{21} = 0.986$
Ethane-*n*-butane	1.482	$A_{13} = 0.849$	$A_{31} = 0.960$
Ethane-*n*-pentane	1.678	$A_{14} = 0.813$	$A_{41} = 0.883$
Propane-*n*-butane	1.181	$A_{23} = 1.017$	$A_{32} = 0.973$
Propane-*n*-pentane	1.338	$A_{24} = 0.914$	$A_{42} = 0.986$
n-Butane-*n*-pentane	1.132	$A_{34} = 1.059$	$A_{43} = 0.955$

These values are substituted into the expanded form of Equation (1) for a quaternary mixture:

$$T_{cm} = \frac{T_{c_1}}{1 + \frac{x_2}{x_1}A_{12} + \frac{x_3}{x_1}A_{13} + \frac{x_4}{x_1}A_{14}} + \frac{T_{c_2}}{1 + \frac{x_1}{x_2}A_{21} + \frac{x_3}{x_2}A_{23} + \frac{x_4}{x_2}A_{24}} + \frac{T_{c_3}}{1 + \frac{x_1}{x_3}A_{31} + \frac{x_2}{x_3}A_{32} + \frac{x_4}{x_3}A_{34}} + \frac{T_{c_4}}{1 + \frac{x_1}{x_4}A_{41} + \frac{x_2}{x_4}A_{42} + \frac{x_3}{x_4}A_{43}}$$

$$T_{cm} = \frac{549.5}{1 + \frac{0.255}{0.254}(0.996) + \frac{0.255}{0.254}(0.849) + \frac{0.236}{0.254}(0.813)} + \frac{666.0}{1 + \frac{0.254}{0.255}(0.986) + \frac{0.255}{0.255}(1.017) + \frac{0.236}{0.255}(0.914)} + \frac{765.7}{1 + \frac{0.254}{0.255}(0.960) + \frac{0.255}{0.255}(0.973) + \frac{0.236}{0.255}(1.059)} + \frac{847.1}{1 + \frac{0.254}{0.236}(0.883) + \frac{0.255}{0.236}(0.986) + \frac{0.255}{0.236}(0.955)} = 734\text{°R.}$$

Etter and Kay (*10*) report a critical temperature of 731°R. for this mixture.

CONCLUSIONS

A direct and accurate method for the prediction of the critical temperatures of multicomponent hydrocarbon systems has been developed. From a knowledge of the normal boiling points and critical temperatures of the pure components the critical temperature of a mixture containing an unlimited number of components may be estimated with an expected error of approximately 1%. The components may be normal paraffins, isoparaffins, olefins, acetylenes, naphthenes, and aromatics and are limited only by the prescribed boiling-point ratio ranges. This approach may be extended to systems containing nonhydrocarbon components once a reasonable quantity of data on such systems becomes available.

NOTATION

A_{ij} = temperature coefficient for binary system consisting of i and j components

n = number of components

T_{b_i} = normal boiling point of ith component, °R.

T_c^* = corrected critical temperature for aromatic component, °R.

T_{c_i} = critical temperature of ith component, °R.

T_{c_m} = critical temperature of mixture, °R.

x_i = mole fraction of ith component

x_j = mole fraction of jth component

τ = normal boiling-point ratio, T_{b_2}/T_{b_1}

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COMMUNICATIONS TO THE EDITOR

A Note on the Method of Moments

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Increasing attention has been devoted to methods of unsteady state analysis in the investigation of various systems of chemical engineering interest. Response analysis techniques are standard methods in feedback control theory, and any system which is rate controlled is subject to such analysis. Analytical solution of the equations of many systems, even though linear, is often formidable, and various alternatives have been used. Characterization of a response function in terms of moments can be useful in some cases and has been discussed by several workers (*1, 2, 3, 5, 7, 9, 10*) after the original suggestions of Van der Laan (*15*). Applications to chemical engineering have been almost exclusively in various discussions of the fixed-bed, axial dispersion problem. Although there are cer-