R & D NOTES

An Alternative Method for the Estimation of Critical Temperatures of Mixtures

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A knowledge of the critical temperature of mixtures is important, and because of the difficulty of measuring the critical properties of mixtures experimentally, it is desirable to have reliable methods for correlating and predicting these properties. A survey of the literature indicates that a variety of correlations have been advanced for predicting the critical temperature of mixtures. For example Spencer et al. (1973) reviewed and evaluated a number of proposed methods for estimating the critical temperatures of mixtures. In this note a new alternative method, based on the heat capacity fraction, is proposed to correlate experimentally determined critical temperatures.

If the composition of a mixture is expressed as

$$\delta i = \frac{Y_i Cv_i}{\Sigma Y_i Cv_i} \qquad (1)$$

the mixture's critical temperature can be estimated by

$$T_{cm} = \Sigma \delta i \, T_{c_i} \qquad (2)$$

where y_i is the mole fraction of i, C_{v_i} the molal heat capacity of i, T_{c_i} the critical temperature of i, and T_{cm} the mixture critical temperature. Here our attention is restricted to normal fluids; that is, to molecules that have zero (or small) dipole moments, no tendency to associate by hydrogen bonding or similar chemical forces, and that have sufficiently large mass to permit neglect of quantum corrections.

In figure 1, the critical temperature of three binary systems—methane-propane (Reamer et al., 1950); methane–*n*-butane (Sage et al., 1940); and methane–*n*-pentane (Sage et al, 1942)—are shown plotted as a function of mole fraction (open symbols) and heat capacity fraction (closed symbols). It is clear that the use of heat capacity fractions provides essentially a linear relationship between δi and T_{cm}, as predicted by Eq. 2. Table 1 lists literature data employed for the calculations.

The behavior of the binary hydrocarbon mixtures that have been investigated raises the possibility of using this nearly linear property to estimate the critical temperature of ternary systems of hydrocarbons. To establish these values only the critical temperature and the molal heat capacity data for each component is required. The approach to the estimation of such temperatures is as follows.

Since the critical temperature is not known, values must be assumed and the answer can be reached by a series of successive approximations. As a starting assumption the molal average pseudocritical temperature of the mixture ($T_{cp} = \Sigma_i y_i T_{c_i}$) can be taken as equal to the temperature sought. This allows us to calculate the heat capacity fraction, Eq. 1, and the desired temperature, Eq. 2. The procedure is repeated until the new calculated value of T_{cm} checks with the last calculated value. The search procedure is straightforward and does not in general require a large number of iterations to find the critical temperature. To illustrate this method of calculation the following example is presented.

Example

Determine the critical temperature of a ternary mixture having the following composition

	Mol Frac.
Methane	0.480
Propane	0.265
n-Pentane	0.255
	1.000

Step A. From the data in Table 1 we calculate the molal average pseudocritical temperature for this mixture. The starting assumption is:

$$T_{cp} = 0.48(190.6) + 0.265(396.8) + 0.255(469.6)$$
$$= 309 \text{ K.}$$

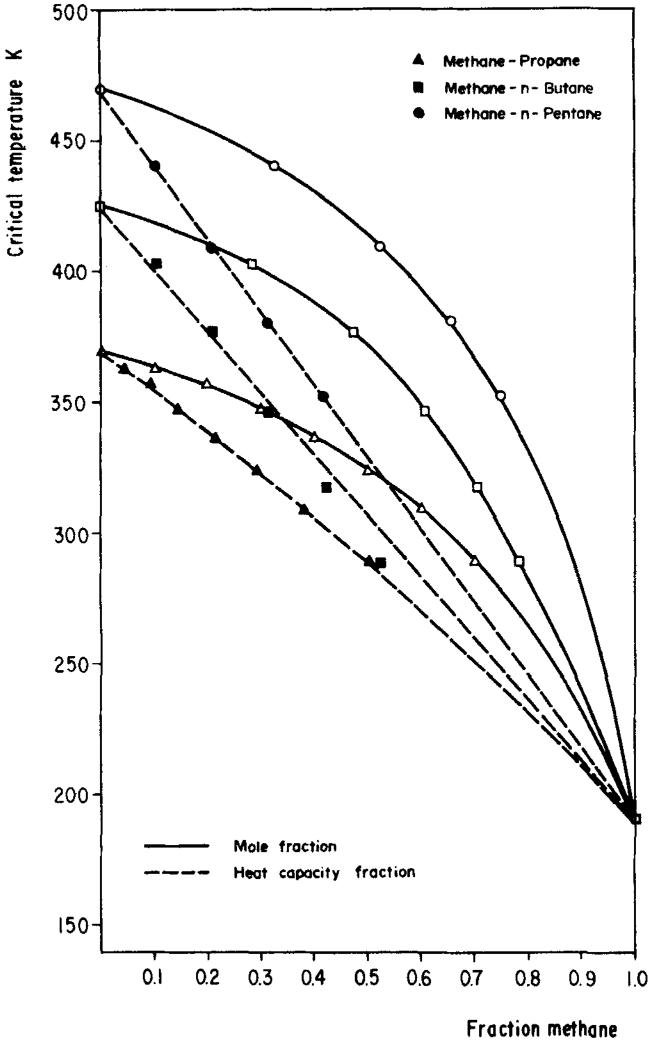

Figure 1. Critical temperatures of three binary methane systems as a function of mole fraction and heat capacity fraction.
△□○ Mole fraction
▲■● Heat capacity fraction.

Table 1. Literature Data for Calculations Plotted in Figure 1 (Reid et al., 1977)

Compound	Crit. Temp. K	Constants in Ideal Gas Heat Capacity Eq.* cal/mol · K		
		A	$B \times 10^2$	$C \times 10^5$
Methane	190.6	2.611	1.245	0.286
Propane	369.8	−2.966	7.315	−3.789
n-Butane	425.2	0.279	7.913	−2.647
n-Pentane	469.6	−2.853	11.64	−6.163

$^*A + BT + CT^2 - R$
R, universal gas constant = 1.987 cal/mol · K

Using Eq. 1:

	C_v at 309 K cal/mol · K	Heat Capacity Frac.
Methane	6.374	0.2239
Propane	16.031	0.2937
n-Pentane	27.248	0.4824
		1.000

With Eq. 2:

$$T_{cm} = 0.2239(190.6) + 0.2937(36.8) + 0.4824(496.6)$$
$$= 377.8 \text{ K}.$$

Step B. At $T = 377.8$ K, using Eq. 1:

	C_v at 377.8 K cal/mol · K	Heat Capacity Frac.
Methane	7,723	0.2171
Propane	19,262	0.2985
n-Pentane	32,326	0.4843
		1.000

With Eq. 2:

$$T_{cm} = 0.2171(190.6) + 0.2985(369.8) + 0.4843(469.6)$$
$$= 379.2 \text{ K}.$$

Step C. At 379.2 K, with Eq. 1:

	C_v at 379.2 K cal/mol K	Heat Capacity Frac.
Methane	7,743	0.2174
Propane	19,324	0.2990
n-Pentane	32,424	0.4836
		1.000

With Eq. 2:

$$T_{cm} = 379.1 \text{ K } (222.4°\text{F}).$$

For this particular ternary composition, Grieves and Thodos (1962) report a critical temperature of 220°F (104°C) × (377.8K).

There is also an alternative procedure to calculate T_{cm}. The heat capacity of each component can be estimated from the principles of statistical mechanics, in which the total internal energy is made equal to the sum of the energies due to the translational and rotational motions of the molecule and to the vibrational motion of the atoms making up the molecules.

The theory of equipartition of energy provides a means of estimating the molal heat capacity of a gas. According to this theory, each translational and rotational degree of freedom contributes $R/2$ to Cv, while the maximum vibrational contribution is R, where R = gas constant. Since, there is a total of $3N$ (N = number of atoms in the molecule) degrees of freedom, the *molal* heat capacity for a nonlinear molecule (three rotational degrees of freedom) becomes:

$$Cv = 3R/2 + 3R/2 + (3N - 6)R = 3(N - 1)R$$

The previously-mentioned example then can be solved by this method. The molal heat capacities and the values of δi, calculated using Eq. 1 are:

	Cv	δi
Methane	$12R$	0.222
Propane	$30R$	0.306
n-Pentane	$48R$	0.472
		1.000

Using Eq. 2, we obtain:

$$T_{cm} = (0.222)(190.6) + (0.306)(369.8) + (0.472)(469.6)$$
$$= 377.1\ \text{K}.$$

This agreed reasonably well with the iterative method described earlier.

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Notation

C_{v_i} = molal heat capacity at constant volume of component i
R = gas constant
T = temperature
T_{c_i} = critical temperature of component i
T_{cm} = critical temperature of a mixture
T_{cp} = pseudocritical temperature
y_i = mole fraction of component i
δi = heat capacity fraction

Subscripts

c = critical
i = pure component i
m = mixture

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