

Correlation of Critical Properties and Acentric Factor of Hydrocarbons and Derivatives

HO-MU LIN and
KWANG-CHU CHAO

School of Chemical Engineering
Purdue University
West Lafayette, IN 47907

The critical constants and acentric factor are generally required in thermodynamic calculations based on the principle of corresponding states. In this work, these properties of hydrocarbons and derivatives are correlated with the molecular weight, specific gravity, and normal boiling point. Properties of n-alkanes are correlated with the molecular weight. Properties of other hydrocarbons and derivatives are expressed as perturbations from those of the n-alkanes, and the perturbations are correlated in terms of specific gravity and normal boiling point.

INTRODUCTION

Corresponding states correlations are in wide use in thermodynamic calculations. Application of the correlations requires the characteristic constants to be known for the substances of interest. The most widely used characterization parameters are the critical constants and the acentric factor. Availability of these properties has been a limitation to the usefulness of the correlations. The heavy hydrocarbons and derivatives decompose at temperatures below the critical, making it impossible to experimentally determine the critical properties. For petroleum and coal liquid fractions the critical constants are also unknown; the critical properties and acentric factor have to be estimated from correlations.

Several correlations of critical properties and acentric factor have been developed. The correlations of Cavett (1962), Kesler-Lee (1976), and Riazi-Daubert (1980) have been in use for petroleum fractions. Recently, Wilson et al. (1981) developed correlations for T_c and P_c , and Brulé et al. (1982) for T_c and V_c based on the data of compounds found in coal liquids. All these methods involve only the boiling point and the specific gravity. Kesler and coworkers (1979) introduced a third parameter, together with boiling point and specific gravity, to correlate T_c , P_c , ω , and the heat of vaporization useful for petroleum fractions. This third parameter requires vapor pressure data at temperature of $0.85 T_b$ which are not available for many heavy components found in coal liquids.

In this work we develop correlations for the critical constants and acentric factor in terms of molecular weight M , normal boiling point T_b , and specific gravity S . Molecular weight has been correlated with T_b and S for petroleum fractions, but the correlation breaks down for nonpetroleum fluids. Since molecular weight is readily determined by experiment, we introduce it as a correlating variable to obtain more general results.

The specific gravity we use here is the ratio of the density of the liquid at 20°C to that of water at 4°C.

In the following development properties of the n-alkanes are correlated with M . Properties of the other hydrocarbons and derivatives are expressed as perturbations to those of the n-alkanes, and the perturbations are correlated with T_b and S .

n-Alkane Correlations

The critical properties and acentric factor of C_1 to C_{20} n-alkanes are correlated with M by the following equations,

$$\Theta_A = C_1 + C_2M + C_3M^2 + C_4M^3 + C_5/M \quad (1)$$

where Θ_A represents either T_c , $\ln P_c$, V_c , or ωT_c of a n-alkane. The coefficients C_1 to C_5 are reported in Table 1 for each property. We have additionally correlated S and T_b of the n-alkanes by Eq. 1, and the coefficients are included in Table 1. The correlated S_A and T_{bA} of the n-alkanes will be required in the perturbation equations to follow as independent variables.

The dimensions of the quantities in Eq. 1 are given in Notation.

The average absolute deviations (AAD) of the correlations from the American Petroleum Institute Project 44 table values are 0.15% for T_c , 1.0% for P_c (excluding methane), 0.8% for V_c , 1.2% for ω , 0.11% for T_b , and 0.07% for S . The specific gravity correlation applies only to C_5 - C_{16} which are the only n-alkanes that are liquids at 20°C. These results are appreciably improved over the correlations of Kesler and coworkers (1979) based on the data of C_5 - C_{15} n-alkanes.

GENERAL CORRELATIONS

Properties of the general hydrocarbons and derivatives are correlated as perturbations of those of n-alkanes according to the equation,

$$\begin{aligned} \Theta = \Theta_A + A_1\Delta S + A_2\Delta T_b + A_3(\Delta S)^2 + A_4(\Delta S)(\Delta T_b) \\ + A_5(\Delta T_b)^2 + A_6(\Delta S)^3 + A_7(\Delta S)^2(\Delta T_b) \\ + A_8(\Delta S)(\Delta T_b)^2 + A_9(\Delta T_b)^3 \quad (2) \end{aligned}$$

with

TABLE 1. COEFFICIENTS FOR Θ_A IN EQ. 1

Θ_A	C_1	C_2	C_3	C_4	C_5
T_c	2.72697×10^2	3.91999	-1.17706×10^{-2}	1.48679×10^{-5}	-2.27789×10^3
$\ln P_c$	1.77645	-1.01820×10^{-2}	2.51106×10^{-5}	-3.73775×10^{-8}	3.50737
V_c	1.54465×10	4.04941	1.73999×10^{-4}	1.05086×10^{-6}	2.99391×10^2
ωT_c	-1.56752×10	1.22751	9.96848×10^{-3}	-2.04742×10^{-5}	-6.90883×10
S	6.64050×10^{-1}	1.48130×10^{-3}	-5.07021×10^{-6}	6.21414×10^{-9}	-8.45218
T_b	1.33832×10^2	3.11349	-7.08978×10^{-3}	7.69085×10^{-6}	-1.12731×10^3

T_c and T_b are in K, P_c in MPa, V_c in cm^3/mol .

TABLE 2. COEFFICIENTS FOR EQ. 2

	T_c	$\ln P_c$	Θ	V_c	ωT_c
a_1	1.58025×10^3	9.71572		-1.18812×10^3	-1.16044×10^3
a_2	-5.68509	-3.32004×10^{-2}		-1.18745	3.48210
a_3	-1.21659×10^4	-8.60375×10		7.36085×10^3	2.78317×10^4
a_4	7.50653×10	5.50118×10^{-1}		6.83380×10	-2.05257×10^2
a_5	-9.66385×10^{-2}	-9.00036×10^{-4}		-2.12107×10^{-1}	4.55767×10^{-1}
a_6	2.17112×10^4	1.85927×10^2		-4.84696×10^3	-7.13722×10^4
a_7	-1.57999×10^2	-1.51115		-4.12064×10^2	5.08888×10^2
a_8	3.60522×10^{-1}	4.32808×10^{-3}		2.02114	-6.10273×10^{-1}
a_9	-2.75762×10^{-4}	-3.81526×10^{-6}		-2.48529×10^{-3}	-1.68712×10^{-3}
b_1	-1.18432×10	-7.50370×10^{-2}		1.17177×10	1.89761
b_2	5.77384×10^{-2}	3.15717×10^{-4}		-3.48927×10^{-2}	2.41662×10^{-2}
b_3	1.10697×10^2	8.42854×10^{-1}		-1.34146×10^2	-2.67462×10^2
b_4	-6.58450×10^{-1}	-5.21464×10^{-3}		5.63667×10^{-2}	2.06071
b_5	7.82310×10^{-4}	7.87325×10^{-6}		9.52631×10^{-4}	-5.22105×10^{-3}
b_6	-2.04245×10^2	-1.85430		1.80586×10^2	7.66070×10^2
b_7	1.32064	1.36051×10^{-2}		2.56478	-5.75141
b_8	-2.27593×10^{-3}	-3.23929×10^{-5}		-1.74431×10^{-2}	8.66667×10^{-3}
b_9	8.74295×10^{-7}	2.18899×10^{-8}		2.50717×10^{-5}	1.75189×10^{-5}

$$\Delta S = S - S_A \quad (3)$$

$$\Delta T_b = T_b - T_{bA} \quad (4)$$

where S_A and T_{bA} are the gravity and boiling point of the hypothetical n-alkane of the M of the substance of interest and are given by Eq. 1.

The coefficients A_i in Eq. 2 are given by

$$A_i = a_i + b_i M \quad (5)$$

Table 2 presents the coefficients a_i and b_i that have been determined by fitting Eq. 2 to the properties of a large number of hydrocarbons and derivatives. The collection of Lin and coworkers (1980a,b,c) provides the basic set of data.

DISCUSSION

Figures 1–4 show comparison of the correlations with literature values for T_c , P_c , V_c , and ω , respectively. Table 3 presents the average deviations of the same comparisons, and the numbers of literature values used in the correlations of the various properties and the average deviations of several other correlations in the literature from the same data set.

The present correlations are found to represent the data reasonably well, and the representation is improved over all previous correlations. The improvement is significant for P_c , V_c , and ω . For T_c all correlations give good results, and the improvement of the present work over previous ones is slight.

The legend of the symbols of the figures are the same and are given in Figure 1. Literature values are classified according to the chemical nature of the substance. The different classes appear to be equally well correlated in Figure 1 except for two nitrogen compounds. Figures 2 and 3 show the correlations of P_c and V_c of the heterocyclics to be more scattered, but no trends are observed. Figure 4 shows more pronounced scattering; a trend for the oxygen heterocyclics and phenols to deviate positively from the correlated ω is also observable. The data for 3,4-xyleneol, 2,4-xyleneol, 2,5-xyleneol, and benzoic acid deviate substantially from the correlation. Their vapor pressures calculated by the correlated ω would be too high. Additional perturbation terms associated with polarity effects seem to be needed for these substances.

Some of the scattering must be due to the uncertainties of the literature values. Lin and coworkers found different values for the same substance in many cases. The ω values, for example, are given as 0.371 and 0.2736 for sec-butyl-benzene, and 0.376 and 0.2647 for tert-butyl benzene. The lower values were used in this work. Critical volumes are correlated to within 5% for the majority of

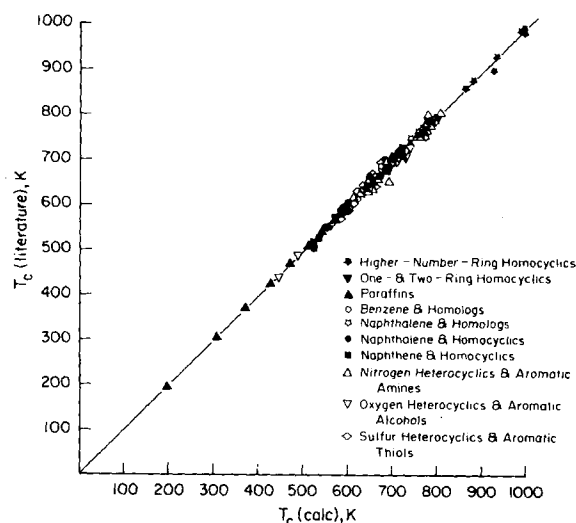


Figure 1. Comparison of correlated critical temperature with literature values.

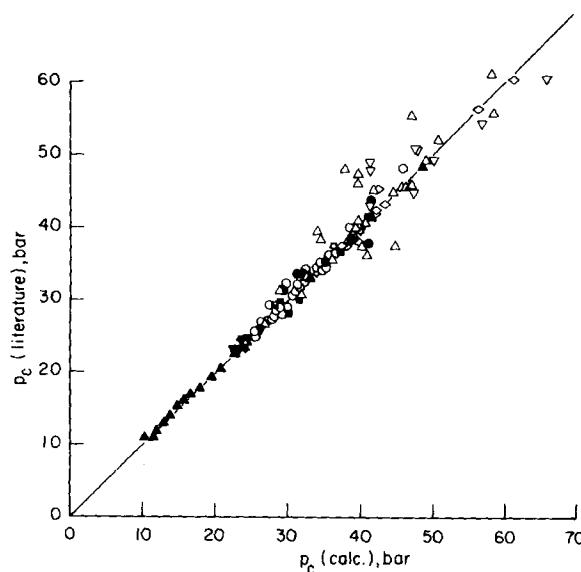


Figure 2. Comparison of correlated critical pressure with literature values.

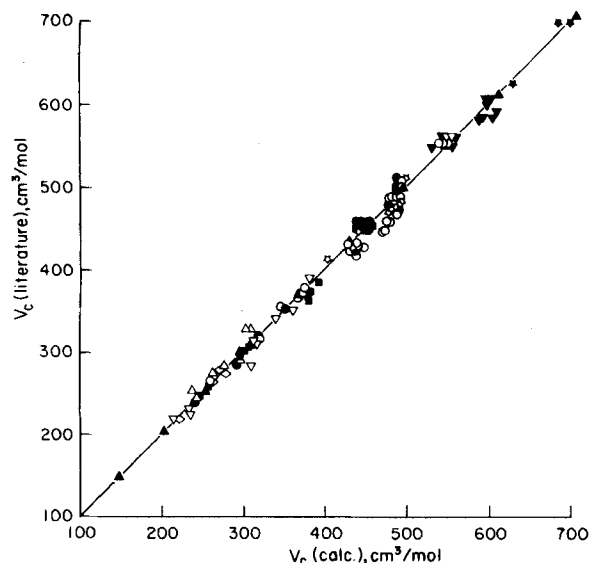


Figure 3. Comparison of correlated critical volume with literature values.

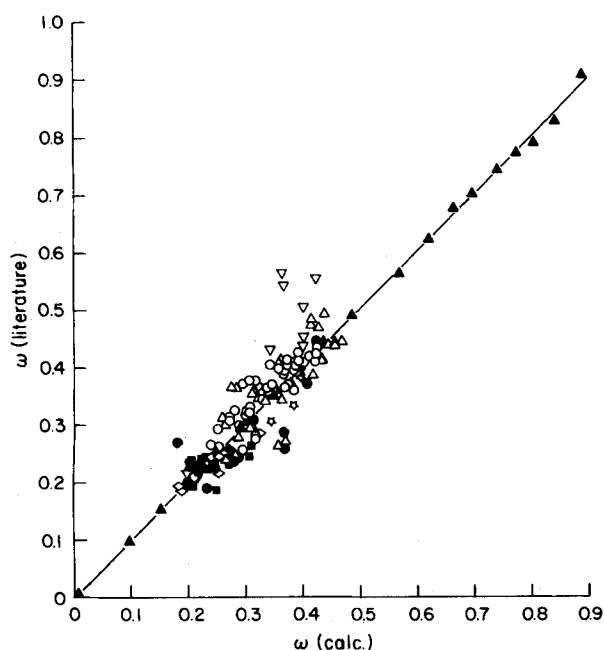


Figure 4. Comparison of correlated acentric factor with literature values.

TABLE 3. COMPARISON OF CORRELATIONS WITH LITERATURE DATA

	No. of Lit. Values Used	Average Absolute Deviation, %				
		This Work	Kesler- Lee	Brulé et al.	Wilson et al.	Riazi and Daubert
T_c	176	1.1	1.7	1.3	2.1	1.9
P_c	165	3.5	8.8	—	9.1	9.9
V_c	122	2.8	—	8.0	—	4.9
ω	133	8.5	20.5	—	—	—

data. Only the values of cis-decalin and o-cresol display large deviations from the correlation. The correlation of P_c shows deviations of more than 10% for pyrrole, p-toluidine, quinaldine, pyrrolidine and 3,4-xyleneol, etc. The AAD is reduced to less than 3% if these data are excluded.

Improved results have been obtained by correlating the product ωT_c in preference to ω by itself. To find ω from the product the correlated T_c may be used although T_c data from the literature were used in the correlation, the difference between the correlated T_c and literature value being quite slight.

ACKNOWLEDGMENT

This work was supported by Electric Power Research Institute through Research Project RP-367.

NOTATION

A, a, b = coefficients in Eq. 2
 C = coefficients in Eq. 1
 M = molecular weight
 P_c = critical pressure, MPa
 S = specific gravity
 T_b = normal boiling point, K
 T_c = critical temperature, K
 V_c = critical volume, cm³/mol
 ω = Pitzer's acentric factor
 Θ = a physical property

Subscript

A = n-alkane

LITERATURE CITED

- Brulé, M. R., C. T. Lin, L. L. Lee, and K. E. Starling, "Multiparameter Corresponding-States Correlation of Coal-Fluid Thermodynamic Properties," *AIChE J.*, **28**, 616 (1982).
 Cavett, R. H., "Physical Data for Distillation Calculations—Vapor-Liquid Equilibria," *Proc. Am. Petrol. Inst.*, Sect. 3, **42**, 351 (1962).
 Kesler, M. G., and B. I. Lee, "Improve Prediction of Enthalpy of Fractions," *Hydroc. Process.*, **55**(3), 153 (Mar., 1976).
 Kesler, M. G., B. I. Lee, and S. I. Sandler, "A Third Parameter for Use in Generalized Thermodynamic Correlations," *Ind. Eng. Chem. Fund.*, **18**, 49 (1979).
 Lin, C. T., et al., "Data Bank for Synthetic Fuels," Part 1, *Hydroc. Process.*, **59**(5), 229 (May, 1980a).
 Lin, C. T., et al., "Data Bank for Synthetic Fuels," Part 2, *Hydroc. Process.*, **59**(8), 117 (Aug., 1980b).
 Lin, C. T. et al., "Data Bank for Synthetic Fuels," Part 3, *Hydroc. Process.*, **59**(11), 225 (Nov., 1980c).
 Riazi, M. R., and T. E. Daubert, "Simplify Property Predictions," *Hydroc. Process.*, **59**(3), 115 (Mar., 1980).
 Wilson, G. M., R. H. Johnston, S. C. Hwang, and C. Tsionopoulos, "Volatility of Coal Liquids at High Temperatures and Pressures," *Ind. Eng. Chem., Process Des. Dev.*, **20**, 94 (1981).

Manuscript received January 31; revision received March 31, and accepted April 5, 1983.