Correlations of Critical Constants with Parachors

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Since the publication of the article, "Correlations of Critical Constants with Parachors" (*1*) more experimental data on critical constants have become available in the literature. Utilizing experimental data from the literature through 1955, the constants for the equations for estimating critical temperature, pressure, and volume have been re-evaluated by the Computer Group at Ethyl Corp., Baton Rouge, La. These new constants give more reliable correlations when applied to all of the data now available. Also, they distribute the range of deviations of calculated critical constants from experimental constants more evenly among the different groups of compounds.

The new constants presented in Tables I, II, and III extend the range of application of Herzog's original correlation between parachors and critical constants, because 12 rather than six groupings of compounds have been recognized.

The new equation constants are based on calculated parachors using the atomic and structural constants of Mum-

Table I. Critical Temperature

Group of Compounds Covered by Equation	Equations Derived by Least Squares	No. of Compounds in Group	Reliability, %
Alkanes (excluding methane)	$T_c/T_B = 2.480 - 0.4030 \log [P]$	38	2.0
Alkenes and alkynes	$T_c/T_B = 2.298 - 0.3199 \log [P]$	18	3.3
Cycloalkanes	$T_c/T_B = 2.679 - 0.4726 \log [P]$	5	2.8
Aromatics	$T_c/T_B = 2.802 - 0.5259 \log [P]$	15	1.2
Ethers	$T_c/T_B = 2.529 - 0.4310 \log [P]$	6	1.6
Ketones	$T_c/T_B = 1.775 - 0.1139 \log [P]$	6	2.9
Acids	$T_c/T_B = 2.335 - 0.3861 \log [P]$	6	1.1
Esters	$T_c/T_B = 2.562 - 0.4522 \log [P]$	12	1.1
Alcohols	$T_c/T_B = 1.544 - 0.0337 \log [P]$	11	4.5
Nitrogen compounds	$T_c/T_B = 2.011 - 0.2166 \log [P]$	17	4.6
Sulfur compounds	$T_c/T_B = 2.698 - 0.4848 \log [P]$	6	3.4
Halogenated hydrocarbons	$T_c/T_B = 2.294 - 0.3224 \log [P]$	32	5.8
Total		172	

Table II. Critical Pressure

Group of Compounds Covered by Equation	Equations Derived by Least Squares	No. of Compounds in Group	Reliability, %
Alkanes (excluding methane)	$\log p_c = 2.784 - 0.5357 \log [P]$	38	8.3
Alkenes and alkynes	$\log p_c = 2.700 - 0.4818 \log [P]$	11	13.0
Cycloalkanes	$\log p_c = 3.596 - 0.8430 \log [P]$	5	4.4
Aromatics	$\log p_c = 3.716 - 0.8785 \log [P]$	14	6.5
Ethers	$\log p_c = 3.582 - 0.8579 \log [P]$	5	23.5
Ketones	$\log p_c = 2.170 - 0.2476 \log [P]$	5	21.7
Esters	$\log p_c = 3.559 - 0.8410 \log [P]$	12	7.9
Alcohols	$\log p_c = 2.614 - 0.3885 \log [P]$	9	18.3
Nitrogen compounds	$\log p_c = 2.470 - 0.3656 \log [P]$	17	34.0
Sulfur compounds	$\log p_c = 3.730 - 0.9034 \log [P]$	6	6.6
Halogenated hydrocarbons	$\log p_c = 2.863 - 0.5470 \log [P]$	29	43.7
Total		151	

Table III. Critical Volume

Group of Compounds Covered by Equation	Equations Derived by Least Squares	No. of Compounds in Group	Reliability, %
Alkanes (excluding methane)	$V_c = 1.301 (P) + 8.469$	37	6.1
Alkenes and alkynes	$V_c = 1.411 (P) - 13.157$	7	3.2
Cycloalkanes	$V_c = 1.254 (P) + 7.658$	5	6.1
Aromatics	$V_c = 1.400 (P) - 25.604$	14	1.1
Ethers	$V_c = 1.324 (P) - 2.569$	6	13.8
Ketones	$V_c = 0.682 (P) + 124.691$	5	16.3
Acids	$V_c = 1.502 (P) - 25.560$	4	0.8
Esters	$V_c = 1.506 (P) - 38.039$	12	3.9
Alcohols	$V_c = 1.109 (P) + 29.638$	5	10.6
Nitrogen compounds	$V_c = 1.070 (P) + 53.263$	8	8.0
Sulfur compounds	$V_c = 1.458 (P) - 29.008$	4	3.1
Halogenated hydrocarbons	$V_c = 1.358 (P) - 9.354$	24	11.5
Total		131	

ford and Phillips, as was done by Herzog in his original article. Constants were also derived for these equations using experimental parachors but no significant improvement in correlation was observed. Hence, it was decided to use the calculated parachors throughout since calculated parachors are normally more convenient to use.

Equations with the re-evaluated constants are shown in Tables I, II, and III, together with their per cent "reliabilities." Reliabilities of the estimated T_c values were calculated using the equation shown below. This equation gives the maximum deviation to be expected in 95% of the cases. The same approach was used in determining the p_c and V_c equation reliabilities.

$$d = 200\sqrt{\frac{1}{n-1}\sum\left(\frac{T_c(\text{exptl.}) - T_c(\text{calcd.})}{T_c(\text{exptl.})}\right)^2}$$

LITERATURE CITED

(1) Herzog, R., *Ind. Eng. Chem.* **36**, 997–1001 (1944).

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Prediction of Compressibility of Natural Gas Mixtures by Use of the Benedict-Webb-Rubin Equation of State

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A knowledge of the pressure-volume-temperature properties of natural gas is of great importance in the transportation, storage, and use of the gas as a fuel and as a source of raw materials for chemical syntheses. Because of the variable composition of natural gas and the time and skill required to determine the P-V-T properties in the laboratory, it has long been the goal of research engineers within the industry to find an accurate method for their calculation. Heretofore, the methods proposed have been of limited application. The tentative standards as set forth by the Natural Gasoline Association of America (*15*) and the California Natural Gasoline Association (*9*, *10*) are either not of sufficient accuracy or are limited to relatively low pressures. Following the pseudo-critical concept of Kay (*13*), and assuming the law of corresponding state valid for any natural gas mixture, Dunkle (*12*) proposed a method using pure methane as the basis for evaluating the compressibility of natural gas mixtures. Dunkle's approach was later used by Zimmerman and Beitler (*16*, *17*). Their method is simple and accurate for most natural gases, and has been adopted by the American Gas Association as a new standard for the natural gas industry (*1*). However when the ethane and/or nitrogen and carbon dioxide contents are high, this method is not so accurate as is generally desired.

The present study was undertaken to test the application of the Benedict-Webb-Rubin equation of state (*4*, *5*) to the prediction of the compressibility of natural gas mixtures and particularly to mixtures of high ethane and/or nitrogen and carbon dioxide content. The study was confined to the gaseous phase in the pressure and temperature ranges usually encountered in its transportation and storage. The data on natural gas mixtures compiled by Zimmerman and Beitler (*16*, *17*) were used for purposes of comparison in the study.

CONSTANTS FOR BENEDICT-WEBB-RUBIN EQUATION OF STATE

Benedict, Webb, and Rubin (*5*) have proposed the following empirical equation for the representation of the P-V-T relations of a pure gas:

Table I. Values of Constants in Benedict-Webb-Rubin Equation of State for Compounds Constituting Natural Gas Mixtures

Units. P = pounds per square inch absolute
T = degrees Rankine (°F. + 459.63)
d = pound-moles per cubic foot
R = 10.7335

	Methane, (*4*)	Ethane, (*4*) Adjusted	Propane, (*4*)	Isobutane, (*4*)	*n*-Butane, (*4*)	Isopentane, (*4*)
B_0	0.682401	1.00554	1.55884	2.20329	1.99211	2.56386
A_0	6,995.25	15,525.3	25,915.4	38,587.4	38,029.6	48,253.6
$C_0 \times 10^{-6}$	275.763	2,194.27	6,209.93	10,384.7	12,130.5	21,336.7
b	0.867325	2.85393	5.77355	10.8890	10.2636	17.1441
a	2,984.12	20,850.2	57,248.0	117,047	113,705	226,902
$c \times 10^{-6}$	498.106	6,279.39	25,247.8	55,977.7	61,925.6	136,025
α	0.511172	1.00044	2.49577	4.41496	4.52693	6.98777
γ	1.53961	3.02790	5.64524	8.72447	8.72447	11.8807

	n-Pentane, (*4*)	*n*-Hexane, (*4*)	*n*-Heptane, (*4*)	Carbon Dioxide, Proposed	Nitrogen, (*8*)
B_0	2.51096	2.84835	3.18782	0.558255	0.652648
A_0	45,928.8	54,443.4	66,070.6	8,192.54	3,973.31
$C_0 \times 10^{-6}$	25,917.2	40,556.2	57,984.0	1,864.48	98.4657
b	17.1441	28.0032	38.9917	1.36384	0.597292
a	246,148	429,901	626,106	10,554.4	1,516.34
$c \times 10^{-6}$	161,306	296,077	483,427	2,959.67	142.564
α	7.43992	11.5539	17.9056	0.193192	0.522851
γ	12.1886	17.1115	23.0942	1.07773	1.35999

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