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Short Communication

An equation of state for some gases

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Abstract

An equation of state proposed by Angus *et al* has been tested for seven hydrocarbons and four non-hydrocarbons at wide ranges of temperature and pressure. It is found to be superior to the Benedict–Webb–Rubin equation of state.

Key words: Equation of state, hydrocarbons, non-hydrocarbons, temperature, pressure.

The development of an equilibrium relation, in the absence of special force fields, among pressure, temperature, and volume is mathematically fascinating. Of the several equations proposed, no single equation of state has been found to be applicable with high precision over a wide range of temperatures and pressures. High precision equations have many arbitrary constants whose number depends primarily upon the density range and in a minor way upon the temperature range. With the improvements in experimental P–V–T techniques the trend in recent years has been towards more complicated equations which can fit the data within the experimental precision.

In this work, an equation of state first proposed by Angus *et al*[1] for ethylene has been tested for other hydrocarbons. The equation modified for computer application is as follows:

$$Z = \sum_{I=1}^{M} \sum_{J=1}^{N} B_{IJ}\, T^{J-2} \rho^{I-2} \tag{1}$$

where Z is the compressibility factor, B_{IJ} are constants, T is the temperature in °K, ρ is the density in mole/cc.

The P–V–T data for various hydrocarbons collected from the literature are fitted to eqn (1) by the method of least squares by minimising the sum of squares of

Table I

Constants B_{IJ} for acetylene and ethylene

I \ J	1	2	3	4
Acetylene				
1.	$0\cdot2294626279532 \times 10^{-4}$	$-0\cdot2682312105598 \times 10^{-6}$	$0\cdot1050716533259 \times 10^{-8}$	$-0\cdot1387940051138 \times 10^{-11}$
2.	$-0\cdot2145948616289 \times 10^{1}$	$0\cdot1023888240093 \times 10^{1}$	$-0\cdot8749530783725 \times 10^{-4}$	$0\cdot1067668272425 \times 10^{-5}$
3.	$-0\cdot2208203687171 \times 10^{6}$	$0\cdot1073472393371 \times 10^{1}$	$-0\cdot2167140179246 \times 10^{1}$	$0\cdot1548798956635 \times 10^{-2}$
4.	$-0\cdot4058035443231 \times 10^{7}$	$0\cdot1915920500834 \times 10^{6}$	$-0\cdot9405643800927 \times 10^{3}$	$0\cdot1325042609817 \times 10^{1}$
5.	$-0\cdot3197893606404 \times 10^{11}$	$0\cdot2909541827526 \times 10^{8}$	$-0\cdot8846875016744 \times 10^{6}$	$0\cdot8909053747026 \times 10^{3}$
6.	$0\cdot4908875008008 \times 10^{12}$	$-0\cdot4591279300502 \times 10^{10}$	$0\cdot1401506622245 \times 10^{8}$	$-0\cdot1351845602464 \times 10^{5}$
7.	$-0\cdot1492005377772 \times 10^{15}$	$0\cdot1461974474991 \times 10^{13}$	$-0\cdot4739687788433 \times 10^{10}$	$0\cdot5073340485555 \times 10^{7}$
8.	$0\cdot6186212565596 \times 10^{16}$	$-0\cdot6004865076526 \times 10^{14}$	$0\cdot1933779048421 \times 10^{12}$	$-0\cdot2064570537134 \times 10^{9}$
Ethylene				
1.	$-0\cdot4444932478423 \times 10^{9}$	$0\cdot4179897783672 \times 10^{-2}$	$-0\cdot1300151546150 \times 10^{-4}$	$0\cdot1339283324313 \times 10^{-7}$
2.	$0\cdot6699416348936 \times 10^{3}$	$-0\cdot5348581872234 \times 10^{1}$	$0\cdot1992674971083 \times 10^{-1}$	$-0\cdot2076966665383 \times 10^{-4}$
3.	$-0\cdot5599999952298 \times 10^{6}$	$0\cdot4517266615494 \times 10^{4}$	$-0\cdot1329712863223 \times 10^{2}$	$0\cdot1343271824207 \times 10^{-1}$
4.	$0\cdot1390044570586 \times 10^{9}$	$-0\cdot1279210226080 \times 10^{7}$	$0\cdot3918148615527 \times 10^{4}$	$0\cdot3978419708280 \times 10^{1}$
5.	$-0\cdot1748365517630 \times 10^{11}$	$0\cdot1751927644908 \times 10^{9}$	$-0\cdot5565140269001 \times 10^{[illegible]}$	$0\cdot5756546734890 \times 10^{[illegible]}$
6.	$0\cdot1215399395554 \times 10^{13}$	$-0\cdot1307764575973 \times 10^{11}$	$0\cdot4274617440099 \times 10^{8}$	$-0\cdot4472203698339 \times 10^{[illegible]}$
7.	$-0\cdot4681965020547 \times 10^{14}$	$0\cdot5169940252239 \times 10^{12}$	$-0\cdot1697439180246 \times 10^{10}$	$0\cdot1775599443052 \times 10^{7}$
8.	$0\cdot7595700304683 \times 10^{15}$	$-0\cdot8227438127016 \times 10^{13}$	$0\cdot2679401260818 \times 10^{11}$	$-0\cdot2786616617741 \times 10^{[illegible]}$

Table II

Range and quality of fit for the equation of state

Substance	No. of data points	Temp. range °K	Pressure range atm.	Sum of squares of deviation	Average absolute deviation %		Maximum deviation %	Sources of P–V–T data (references)	Values of M and N	
					Present work	B–W–R equation			M	N
Hydrocarbons										
Acetylene	205	170–320	1–100	$0{\cdot}556 \times 10^{-5}$	0·016	0·152	0·093	2	8	4
Ethylene	352	273–423	1–3155	$0{\cdot}267 \times 10^{-2}$	0·139	0·193	4·283	3, 4	8	4
Propylene	214	298–423	1–2832	$0{\cdot}147 \times 10^{-1}$	0·272	0·900	16·940	5	8	4
Methane	118	273–423	1–257	$0{\cdot}860 \times 10^{-4}$	0·027	1·120	−0·881	6	8	4
Ethane	174	310–510	1–680	$0{\cdot}867 \times 10^{-3}$	0·174	1·260	1·309	7	8	4
Propane	520	243–609	1–680	$0{\cdot}450 \times 10^{-2}$	0·270	1·790	3·598	8 to 11	8	4
n-Butane	312	272–555	1–300	$0{\cdot}158 \times 10^{-2}$	0·191	1·200	−2·021	12	8	4
Non-hydrocarbons										
Hydrogen chloride	273	333–673	56–2011	$0{\cdot}232 \times 10^{-2}$	0·318	1·620	2·863	13	8	4
Ammonia	405	300–580	1–1100	$0{\cdot}262 \times 10^{-2}$	0·264	0·670	−2·439	2	8	3
Sulphur dioxide	463	283–523	0·5–315	$0{\cdot}119 \times 10^{-1}$	0·487	1·200	−9·779	14	8	6
N_2O_4-NO_2-NO-O_2 system	122	294–444	1–136	$0{\cdot}549 \times 10^{-2}$	0·358	1·210	4·035	15, 16	8	6

deviation in compressibility. A computer program for the determination of the constants B_{IJ} and the value of M and N which minimises the sum of squares of deviation has been developed. For the solution of simultaneous equations, the usual Gauss-elimination method is used. All the calculations are performed in double precision arithmetic thereby minimizing the errors in round off and truncation. The values of M and N which give relatively small values of the sum of squares of deviation and the average absolute deviation is chosen as the best. The constants B_{IJ} for the best set of M and N are given for acetylene and ethylene in Table I.

The range and quality of fit of eqn (1) for various substances are tabulated in Table II*.

Equation (1) is found to be far superior to the Benedict–Webb–Rubin equation of state. Although equation (1) has a large number of constants, the accuracy with which the equation fits the P–V–T data warrants the use of this equation of state. Furthermore, this equation of state covers a wide range of temperature and pressure and can be easily handled on a digital computer.

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* The constants B_{IJ} for best values of M and N for all substances are available with the authors.

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