Compressibility Factor of Fuel Gases at 60° F. and 1 Atm.

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MODERN analytical techniques have markedly improved the accuracy with which the composition of a gas can be measured. For many years fuel gases were analyzed by the Orsat or Podbielniak volumetric techniques. Heating values and specific gravities were also determined at atmospheric conditions for pure components and fuel gas mixtures, thus resulting in real gas values. However, because of low accuracy in the analytical methods, particularly with respect to determination of the heavier hydrocarbons, differences between calculated and observed heating values were generally ascribed to experimental techniques, and not interpreted on the basis of gas law deviations.

With the advent of the mass spectrometer and gas chromatograph, more accurate and complete analyses of gas mixtures may be obtained. These analyses can be made on a true mole fraction, or ideal gas, basis. Also, accurate ideal gas heat of combustion values can now be derived from the work of Rossini and others, API Project 44 (*16*). However, full utilization of this improved accuracy cannot at present be obtained in the calculation of real gas heating values and specific gravities. The lack of sufficient data to permit accurate prediction of the compressibility factor for real gas mixtures may result in significant differences between measured values and those calculated from gas analysis. Largest deviations occur in fuel gases containing appreciable quantities of heavier constituents.

Therefore, an experimental program was planned to obtain compressibility factor data at 60° F. and 1 atm. on fuel gas components and mixtures. It was anticipated that these data would provide the basis for development of generalized procedures for prediction of compressibility factors of gas mixtures.

Methods used for the determination of gas compressibility factor fall into two groups: gas density, and pressure-relative volume measurement. In the first group of methods, gas density is measured by gas balance or by direct weighing in a bulb. The accuracy of this method depends on absolute values of pressure, volume, and temperature.

In the second group of methods, measurements of pressure and relative volume are made over a range of pressure, and pV or a related parameter is extrapolated to zero pressure, as in the Burnett method (*2*). A method of this kind for use at pressures near atmospheric was described by Jessen and Lightfoot (*9*). Data are obtained at two or three different pressures by confining the gas sample in progressively larger volumes over mercury. The compressibility factor is calculated by fitting the pV measurements (V is the measured volume here) with an equation such as:

$$pV = (pV)_0 z = (pV)_0 (1 + \beta p) \tag{1}$$

Accuracy depends primarily on relative volume and pressure measurements, and constancy of temperature, rather than on absolute values of these quantities. Absolute values of pressure and temperature affect the result in a much less critical way—that is, by variation of z, rather than of pV and RT, with pressure and temperature. Similarly, the accuracy of z for mixtures is not affected by the dependence of gas density on composition. However, the method is dependent on the linearity of z with pressure.

According to expressions for virial coefficients derived from statistical mechanics, the second virial coefficient, B, in the equation:

$$pV = \mathrm{RT}\,(1 + Bp + Cp^2 + \ldots) \tag{2}$$

represents deviation from ideal behavior involving collisions between two molecules (*8*). From this theory it also follows that the second virial coefficient for mixtures involves only binary interaction terms, and is of the form:

$$B_m = \sum_i x_i^2 B_i + 2\sum_{i \neq j} x_i x_j B_{ij} \tag{3}$$

where x_i is the mole fraction and B_i is the second virial coefficient of the ith pure component, and B_{ij} is the interaction coefficient of components i and j. The latter can be evaluated by experimental determinations of B_m on binary mixtures, together with knowledge of the B_i's. The effect of the third virial coefficient at 1 atm. is very small and is considered later.

Components that normally occur in one or more utility fuel gas in concentrations of 5% or more include methane, ethane, propane, ethylene, propene, nitrogen, air, carbon dioxide, carbon monoxide, and hydrogen. Minor amounts of C_4 and C_5 hydrocarbons also occur, together with traces of heavier hydrocarbons. A review of the literature indicated that sufficiently reliable values of atmospheric pressure compressibility factors were not available for some components, particularly the higher boiling hydrocarbons. Furthermore, only very limited data were available on mixtures of these components at low pressures.

Therefore, compressibility factor measurements were made on a number of pure components, and on a series of selected mixtures. The interaction coefficients among the components that normally occur together in major concentrations were determined. A number of selected major-minor interaction coefficients were also determined to provide a basis for prediction of other coefficients.

APPARATUS

The apparatus is shown in Figure 1. The mixture preparation system, gas expansion system, mercury reservoir, and the lower part of the mercury manometer, are mounted in a water bath with a plate-glass front. The temperature of the bath was maintained within 0.05° of 15.55° C. (60° F.), and did not vary more than 0.01° C. during any one run.

A and *B* are Hoke stainless steel cam-closing valves. Connection to glass parts is made through stainless steel Swagelok fittings and ⅛-inch stainless steel tubing sealed to the glass with Dekhotinsky cement. Other valves are Hoke toggle or needle valves. The upper part of the long manometer arm extends out of the bath and is equipped with a jacket for water circulation. Manometer arms and jacket are constructed of precision bore tubing; arms 1 and 2, 12 mm. in I.D.,; arm 3, 13.8 mm. in I.D. Vacuum is maintained at 0.02 mm. or less with a mechanical vacuum pump and dry ice cold trap, and is read with a tilting McLeod gage sensitive to 0.01 mm. of Hg. Mercury levels are read to 0.05 mm. with a Gaertner 100-cm. cathetometer.

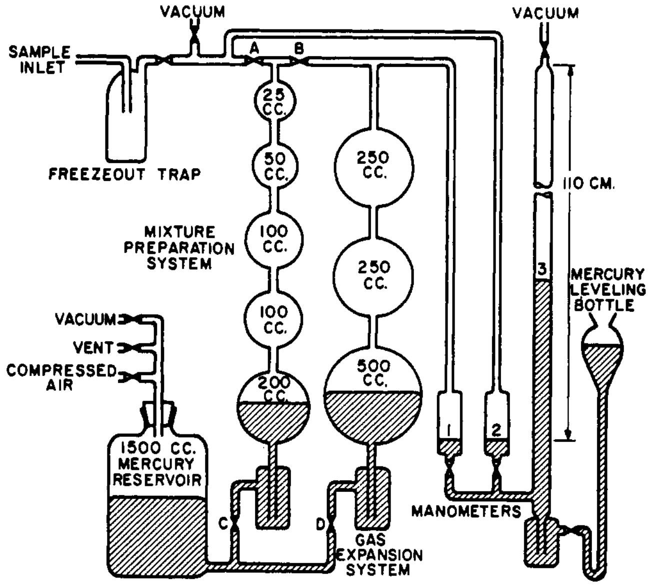

Figure 1. Schematic diagram of low-pressure *P-V* apparatus with integral volumetric mixture preparation system

The mixture preparation bulbs, gas expansion bulbs, and manometer arm 1 were calibrated by weight of mercury delivered. The volume of valve *B* and the capillary manifold in the expansion system, and the volume between valves *A* and *B* and the top of the upper bulb in the mixture preparation system, were determined with a 10-cc. gas buret. The volume between the top and bottom menisci of the manometer arm 1, and corrections for capillary depression, were taken from Kistemaker (*10, 11*).

MATERIALS

The hydrocarbons (Phillips research grade) had a purity of 99.9% or better, except for methane, which was 99.68 mole %, with impurities of ethane and nitrogen. Nitrogen was Matheson prepurified; hydrogen, electrolytic grade from National Cylinder Gas Co. Carbon monoxide (Matheson C.P.) contained 0.3% of oxygen, 0.1% of carbon dioxide, and 0.1% of nitrogen, according to mass spectrometric and gas chromatographic analyses. Components boiling higher than methane were condensed in the freezeout trap to remove air. The part of the apparatus to be filled was flushed with the component.

PROCEDURE

To prepare binary mixtures, the first component was measured in the gas expansion system. The second component was measured in the mixture preparation system by means of manometer arms 2 and 3. The valve *A* was closed and the gases were mixed by being forced from one buret to the other several times. A similar procedure was followed in preparation of multicomponent mixtures, except that the intermediate components were measured one at a time in the mixture preparation buret and transferred to the gas expansion buret. Gas remaining in the section between valves *A* and *B* after transfer was discarded.

In most cases, the two upper bulbs of the gas expansion buret were filled to a pressure of about 950 mm. of Hg. Three to five readings of the top and bottom of the mercury menisci in the two arms of the manometer, and of a reference point on manometer arm 1, were taken. The position of the mercury was changed 1 mm. or so for each reading, to minimize the effect of local imperfections of the manometer tubing and plate glass window. Similar readings were taken after the gas was expanded to fill all three bulbs. Measurements on C_5 hydrocarbons had to be taken at lower pressures; a maximum of about 80% of saturation pressure was used.

The apparatus was constructed with three bulbs to allow measurements at three different pressures on the same charge of gas in order to detect variation of the slope β in Equation 1 with pressure. However, from variances of pV measurements at different pressures, it was concluded that better accuracy might be obtained if only the larger volumes were used, since volume measurement as well as pressure measurements contributed to the error. Accordingly, data at lower pressures was obtained by removing part of the sample and repeating measurements on the same two combinations of bulbs.

Data were fitted to Equation 1 by least squares computation on an Alwac III digital computer.

COMPRESSIBILITY FACTORS OF PURE COMPONENTS

Results for the coefficient β (Equation 1) obtained on pure components are presented in Table I. Determinations at lower pressures were made as a part of runs 2 and 6 on *n*-butane, and of runs 3 and 4 on isobutane, to detect the change of coefficient with pressure. A trend in the direction of smaller numerical values of the coefficient at lower pressures is evident. Such tests were confined to the C_4 hydrocarbons, since the effect is barely detectable with them, and is likely to be less with lighter hydrocarbons and with mixtures. Determination on the C_5 hydrocarbons at necessarily lower pressures would not yield significant results on this question.

The third virial coefficient was introduced to account for the observed trend of β with pressure, and to obtain the best value of $1 - z$ at 1 atm. and 60° F.:

$$pV/(pV)_0 = z = 1 + Bp + Cp^2 \qquad (4)$$

An approximation formula was derived from which values of B and C/B could be evaluated from two measured values of β, and the average initial and final pressures, p_1 and p_2, of each run:

$$B = \beta\,[1 - C/B\,(p_1 + p_2)] \qquad (5)$$

The ratio C/B was evaluated by application of Equation 5 to the data from pairs of runs on the same sample, one made at normal pressures and the other at about half the normal pressures. Runs 2a with 2c, and 6a with 6c, on *n*-butane, and runs 3a with 3b, and 4a with 4b, on isobutane, give C/B ratios of 0.016, 0.007, 0.014, and 0.026, respectively. The average of the four, weighted according to the variance of pV measurements, was 0.016; its standard deviation, also calculated from the variance of pV measurements, was 0.006.

It was desirable to apply similar corrections to the results for other hydrocarbons and mixtures. However, the C/B ratio for lighter gases at 60° F. is smaller than those observed for the butanes—e.g., ethane, 0.006 (*1*)—while higher ratios are theoretically expected for heavier hydrocarbons (*4*). The observed ratio of C/B for the butanes was approximately equal to $B/2$. In order to correct our results on a consistent basis over the complete range of deviations, a C/B ratio of $B/2$ was adopted for all hydrocarbons and mixtures.

Results of determinations of the gas law deviations of the pure component *n*-butane, isobutane, *n*-pentane, isopentane (for the hypothetical gas in the latter two cases), ethylene, and propene are reported in Table I in the form of $1 - z$ for easy comparison with the uncorrected β values. The uncertainties shown are estimated standard deviations. The greater part of the uncertainty with the butanes results from uncertainty of the third virial correction. With pentanes this is overshadowed by the uncertainty of pV

Table I. Experimental Data on Gas Law Deviations of Hydrocarbons at 60° F.

Run No.	β, Atm.$^{-1}$	$p_1 + p_2$, Atm.	Atmospheric Gas Law Deviation, $b = 1 - z$
n-Butane			
1	−0.03413	1.901	0.03361
2a	−0.03466	1.826	0.03417
2b	−0.03433	1.437	0.03410
2c	−0.03422	1.044	0.03419
3	−0.03423	1.849	0.03374
4	−0.03453	1.830	0.03404
5	−0.03411	1.846	0.03362
6a	−0.03437	1.862	0.03387
6b	−0.03397	1.458	0.03370
6c	−0.03416	1.027	0.03414
		Weighted av.	0.03394 ± 0.0002
Isobutane			
1	−0.03022	1.894	0.02982
2	−0.02993	1.891	0.02953
3a	−0.03013	1.889	0.02973
3b	−0.02973	0.937	0.02970
4a	−0.03022	1.881	0.02982
4b	−0.02942	0.895	0.02947
		Weighted av.	0.02971 ± 0.0002
n-Pentane			
1	−0.05504	0.578	0.05570
2	−0.05632	0.525	0.05703
		Weighted av.	0.0565[a] ± 0.0007
Isopentane			
1	−0.05199	0.723	0.05236
2	−0.05076	0.766	0.05107
		Weighted av.	0.0518[a] ± 0.0005
Ethylene			
1	−0.00603	1.917	0.00601
2	−0.00600	1.880	0.00598
		Weighted av.	0.00599 ± 0.00014
Propene			
1	−0.01615	1.887	0.01603
2	−0.01639	1.895	0.01627
		Weighted av.	0.01614 ± 0.00014

[a] For hypothetical gas.

measurements at low pressures. Neither of these sources is very significant in determinations on ethylene and propene, and the uncertainty here was estimated from the pooled variance of the $1 - z$ values from all determinations on butanes, ethylene, and propene. Literature values of the deviations of these hydrocarbons determined at 60° F. are not available; however, in Table II, interpolated values are quoted from the literature or have been calculated from literature values at other temperatures for *n*-butane, propene, and ethylene.

BINARY INTERACTION COEFFICIENTS

Interaction coefficients determined by measurement of the compressibility factors of binary mixtures of components are presented in Table III. These have been calculated by means of the mixture rule of Equation 3, but with the gas law deviation $b = 1 - z$ rather than actual second virial coefficients. Since the third and higher virial coefficients make only a small contribution to the deviation, error from this approximation should not be significant. Values of pure component deviations adopted for calculation of interaction coefficients are given in Table IV.

Duplicate determinations, including preparation of a second mixture, were made in all cases. Estimated standard deviations of the methane–*n*-butane and methane–*n*-pentane average interaction coefficients are 0.00034 and 0.00045, respectively. The standard deviation of other coefficients, estimated from the variance of duplicate determinations, is 0.00019. Since each duplicate determination was made immediately after the first, this estimate may not reflect all sources of error.

Agreement of experimental gas law deviations with the mixture rule was tested by determinations of interaction coefficients on 1:3 and 3:1 mixtures of the methane–*n*-butane, carbon dioxide–*n*-butane, and hydrogen–*n*-butane systems. These mixtures were chosen as most likely to show disagreement. The average interaction coefficient for each system was calculated, with suitable weighting, from all determinations made on the system. The curves obtained from these average interaction coefficients, and the experimental determinations, are shown in Figure 2. Differences between determined values and values calculated from the composition and average interaction coefficient were also calculated. Among all three systems, with a total of 16 mixtures, the maximum deviation was 0.06%, and the standard deviation was 0.028% of the compressibility factor. On the methane–*n*-butane system, a trend of increasing interaction coefficient with increasing methane content is noticeable; however, the difference between 3:1 and 1:3 coefficients is not significant at the 90% confidence level.

COMPLEX MIXTURES

Calculation of compressibility factors by means of interaction coefficients becomes lengthy for routine use on complex mixtures. Calculation of a nine-component mixture, for example, requires nine pure-component terms and 36 interaction terms. Calculation can be simplified, and, in effect, unknown interaction coefficients can be predicted, if the linear square root combination of pure component deviations is valid:

$$b_m = [\sum_i x_i\,(b_i)^{1/2}]^2 = \sum_i x_i^2 b_i + 2\sum_{i\neq j} x_i x_j (b_i)^{1/2}\,(b_j)^{1/2} \qquad (6)$$

Comparison with Equation 3 indicates that interaction coefficients for a given component *i* should lie on a straight line of slope $(b_i)^{1/2}$ if plotted against $(b_j)^{1/2}$. This plot is shown in Figure 3. Experimental points fall reasonably

Table II. Comparison of Experimental and Literature Values of Gas Law Deviations

Gas Law Deviation at 60° F. and 1 Atm., $1 - z$

Component	Present Work	Other Values	
n-Butane	0.03394 ± 0.0002	0.0333	Miller and Rossini (*14*)
		0.0334	Silberberg, Kuo, and McKetta (*17*)
Ethylene	0.00599 ± 0.00014	0.0061[a]	Michels and Geldermans (*13*)
		0.0063[b]	Cawood and Patterson (*3*)
		0.0056	Miller and Rossini (*14*)
Propene	0.01614 ± 0.00014	0.0161	Farrington and Sage (*6*)
		0.0159	Roper (*15*)
		0.0161	Miller and Rossini (*14*)

[a] From plot of values at 0°, 25°, and 50° C. [b] From linear interpolation between values at 0° and 21° C.

Table III. Compressibility Factors and Interaction Coefficients of Binary Mixtures of Fuel Gas Components

Mixture	Composition, Mole % First Component	Gas Law Deviation, b_m[a]	Interaction Coefficient, b_{12}[a]
Methane-ethylene	50.34	0.00353	0.00314
	49.84	0.00340	0.00284
		Av.	0.00299
Methane-ethane	50.58	0.00472	0.00436
	50.70	0.00441	0.00376
		Av.	0.00406
Methane-propane	49.66	0.00798	0.00590
	50.33	0.00771	0.00558
		Av.	0.00574
Methane-isobutane	48.55	0.01155	0.00649
	49.90	0.01137	0.00688
		Av.	0.00668
Methane–*n*-butane	72.14	0.00702	0.00846
	74.79	0.00626	0.00809
	75.11	0.00583	0.00711
	48.47	0.01326	0.00762
	48.72	0.01323	0.00775
	23.58	0.02251	0.00721
	23.72	0.02190	0.00569
	24.59	0.02174	0.00634
		Weighted av.	0.00737
Methane-isopentane	59.83	0.01345	0.00917
	59.71	0.01358	0.00933
		Av.	0.00925
Methane–*n*-pentane	59.18	0.01542	0.01105
	60.48	0.01479	0.01105
	59.89	0.01544	0.01180
		Weighted av.	0.01132
Ethane-propane	50.52	0.01266	0.01222
	50.15	0.01239	0.01162
		Av.	0.01192
Ethane–*n*-butane	49.94	0.01830	0.01542
	49.77	0.01859	0.01592
		Av.	0.01567
Propylene-propane	49.50	0.01707	0.01708
	50.40	0.01701	0.01700
		Av.	0.01704
Propylene-isobutane	50.05	0.02203	0.02120
	49.84	0.02219	0.02144
		Av.	0.02132
Propylene–*n*-butane	49.96	0.02367	0.02232
	50.18	0.02341	0.02190
		Av.	0.02211
Propane–*n*-butane	50.42	0.02504	0.02426
	49.55	0.02499	0.02388
		Av.	0.02407
Nitrogen-methane	50.04	0.00091	0.00072
	50.56	0.00093	0.00078
		Av.	0.00075
Nitrogen-ethane	50.12	0.00344	0.00254
	50.26	0.00334	0.00236
		Av.	0.00245
Nitrogen-propane	48.22	0.00682	...
	48.22	0.00650	...
	48.22	0.00682	...
	Av.	0.00671	0.00362
	49.71	0.00620	0.00334
		Av.	0.00348
Nitrogen–*n*-butane	49.76	0.01039	0.00352
	49.28	0.01070	0.00382
		Av.	0.00367
Air-propene	50.39	0.00546	0.00280
	49.58	0.00557	0.00276
		Av.	0.00278
Air-propane	49.92	0.00577	0.00232
	49.52	0.00606	0.00274
		Av.	0.00253
Air-isobutane	49.39	0.00937	0.00332
	49.44	0.00918	0.00298
		Av.	0.00315
Air–*n*-butane	49.36	0.01038	0.00318
	49.02	0.01050	0.00321
		Av.	0.00320
Air–*n*-pentane	65.83	0.00928	0.00556
	65.55	0.00871	0.00403
	65.15	0.00865	0.00357
		Av.	0.00409
Carbon monoxide–methane	49.86	0.00073	0.00026
	49.70	0.00078	0.00036
		Av.	0.00031
Carbon monoxide–ethylene	50.13	0.00229	0.00136
	49.38	0.00233	0.00136
		Av.	0.00136
Carbon monoxide–propylene	49.26	0.00548	0.00246
	49.68	0.00562	0.00284
		Av.	0.00265
Carbon dioxide–methane	49.64	0.00318	0.00260
	49.49	0.00323	0.00270
		Av.	0.00265
Carbon dioxide–ethane	49.46	0.00630	0.00552
	49.09	0.00602	0.00494
		Av.	0.00523
Carbon dioxide–propane	49.03	0.00977	0.00744
	50.06	0.00992	0.00800
		Av.	0.00777
Carbon dioxide–*n*-butane	74.51	0.00924	0.00975
	49.46	0.01498	0.00990
	50.17	0.01456	0.00942
	24.64	0.02322	0.01021
		Weighted av.	0.00978
Carbon dioxide–nitrogen	49.56	0.00220	0.00144
	50.03	0.00259	0.00218
		Av.	0.00181
Hydrogen-methane	50.26	0.00026	−0.00012
	49.80	0.00000	−0.00066
		Av.	−0.00039
Hydrogen-ethylene	49.57	0.00111	−0.00054
	50.00	0.00100	−0.00070
		Av.	−0.00062
Hydrogen-ethane	51.03	0.00164	−0.00042
	50.81	0.00162	−0.00052
		Av.	−0.00047
Hydrogen-propylene	49.48	0.00358	−0.00076
	49.96	0.00365	−0.00046
		Av.	−0.00061
Hydrogen-propane	50.51	0.00412	−0.00028
	50.07	0.00424	−0.00020
		Av.	−0.00024
Hydrogen–*n*-butane	27.52	0.01767	−0.00023
	49.11	0.00850	−0.00028
	49.58	0.00809	−0.00076
	76.15	0.00162	−0.00011
		Weighted av.	−0.00039
Hydrogen–*n*-pentane	64.41	0.00664	−0.00059
	65.27	0.00646	−0.00022
		Av.	−0.00041

[a] $b_m = x_1^2 b_1 + 2x_1x_2b_{12} + x_2^2 b_2$ where b_m, b_1, b_2 are gas law deviations $(1 - z)$ at 1 atm. for the mixture, pure component 1, and pure component 2, respectively, at mole fractions x_1 and x_2 of components in mixture.

close to the predicted value, except for carbon dioxide and hydrogen mixtures. The anomalous behavior of carbon dioxide, in contrast to that of light hydrocarbons, has also been observed at higher pressures when the Benedict-Webb-Rubin equation is fitted to data on carbon dioxide mixtures (5). In order to retain the advantages of the linear square root combination for calculation of the compressibility factor of complex mixtures, a pseudo *b* value,can be used over a limited range of composition. With common utility fuel gases a pseubo *b* value of 0.0041 for carbon dioxide yields compressibility factors within 0.03% of those calculated with the interaction coefficient. With other mixtures the deviation may be greater, up to 0.16% for pure carbon dioxide.

The linear square root combination breaks down when applied to hydrogen, since its deviation is opposite in sign

Table IV. Gas Law Deviations of Fuel Gas Components at 60° F. and 1 Atm.

Component	Gas Law Deviation, $b = 1 - z$	Source
Methane	0.0019	API (*1*)
Ethane	0.0084	API (*1*)
Propane	0.0180	API (*1*)
n-Butane	0.0339	IGT[b]
Isobutane	0.0297	IGT
n-Pentane	0.0565[a]	IGT
Isopentane	0.0518[a]	IGT
Ethylene	0.0060	IGT
Propene	0.0161	IGT
Air	0.00041	NBS (7)
Carbon dioxide	0.00568	NBS (7)
Carbon monoxide	0.00047	NBS (7)
Hydrogen	−0.00060	NBS (7)
Nitrogen	0.00027	NBS (7)

[a] For the hypothetical gas. [b] Institute of Gas Technology.

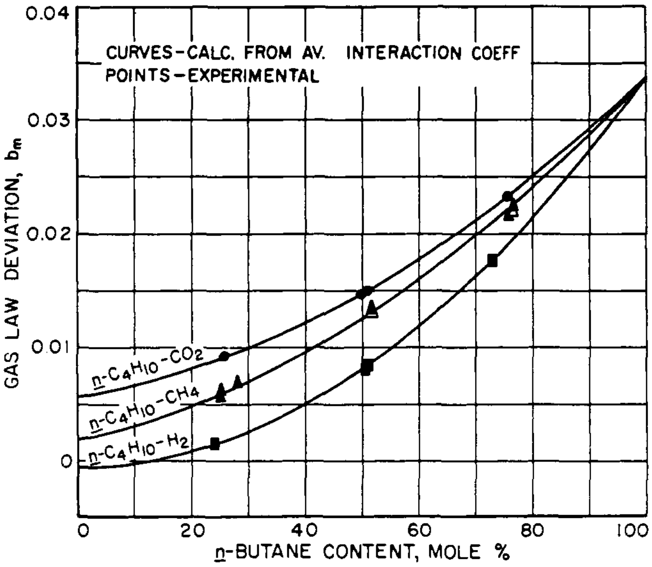

Figure 2. Gas law deviation of *n*-butane mixtures

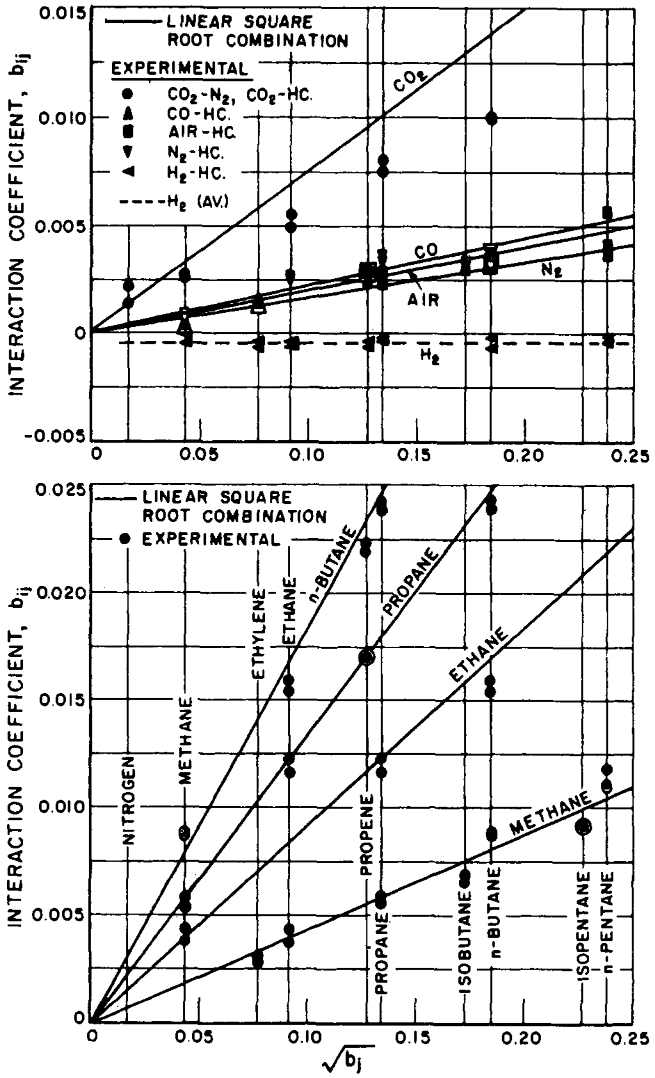

Figure 3. Comparison of experimental and calculated interaction coefficients of nonhydrocarbon-hydrocarbon and carbon dioxide–nitrogen mixtures (top), and hydrocarbon mixtures (bottom)

to that of other components. Data show that its interaction coefficients are negative and substantially constant; the average of determined values is -0.00045. Coefficients for interaction of hydrogen with nitrogen, carbon monoxide, and carbon dioxide were calculated by the method described by Hirschfelder, Curtiss, and Bird (*8*), and were also found to agree well with this average—namely, −0.00053, −0.00052, and −0.00025, respectively. If in the mixture rule, Equation 3, the square root combination is substituted for all components other than hydrogen, and the average value is used for hydrogen interaction coefficients, then:

$$b_m = [\sum x_i(b_i)^{1/2}]^2 + 2x_H\,(1 - x_H)\,(-0.00045) + x_H^2 b_H \qquad (7)$$

where x_H is the mole fraction of hydrogen. Since b_H for hydrogen is −0.0006, a weighted average value −0.0005 may be conveniently substituted for both b_H and the average hydrogen interaction coefficient to obtain:

$$b_M = [\sum x_i\,(b_i)^{1/2}]^2 - 0.0005\,(2x_H - x_H^2) \qquad (8)$$

or

$$z = 1 - [\sum x_i(b_i)^{1/2}]^2 + 0.0005\,(2x_H - x_H^2) \qquad (9)$$

Two four-component mixtures were prepared and their gas law deviations measured to test methods of prediction of the compressibility factors of complex mixtures. The measured values are presented in Table V, together with values calculated by:

1. Linear combination of gas law deviations of components.
2. Mixture rule with binary interaction coefficients, Equation 3.
3. Linear square root combination of gas law deviations of pure components, Equation 6, with the pseudo deviation for carbon dioxide.

These results indicate that the compressibility factor of fuel gas mixtures can be calculated by either 2 or 3 with an accuracy of 0.03% or better. This represents a distinct improvement over the linear combination.

Heating values of gas mixtures are sometimes calculated by summation of terms of the form x_iH_n, where H_n is the real gas heating value of the pure component. This formula yields values for the two mixtures in Table V which are about 3 B.t.u. per standard cu. foot (30 inches of Hg., 60° F.), or almost 0.3% too high. As a result of this study it is recommended that specific gravity and heating value be calculated on the basis of the ideal gas values, and be corrected for nonideality by the mixture compressibility factor. Details of such a procedure are presented in another publication (*12*).

Table V. Gas Law Deviations of Four-Component Mixtures at 60° F. and 1 Atm.

		Mixture	
Component, Mole %		1	2
Methane		67.44	64.14
Ethane		16.37	20.68
Propane		5.30	5.02
Nitrogen		10.89	0.00
Carbon dioxide		0.00	10.16
b_m measured		0.00274	0.00331
b_m calculated[a]	(1)	0.00364	0.00444
	(2)	0.00292	0.00357
	(3)	0.00284	0.00362

[a] b_m calculated from (1) $b_m = \sum x_i b_i$. (2) $b_m = \sum x_i^2 b_i + \sum 2 x_i x_j b_{ij}$. (3) $b_m = [\sum x_i (b_i)^{1/2}]^2$, with pseudo b value 0.0041 for carbon dioxide.

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Supersaturation of Oxygen in Aqueous Hydrogen Peroxide Solutions

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SEVERAL experimental studies on hydrogen peroxide have been misinterpreted because the researcher did not realize that the liquid can become supersaturated with oxygen. For example, recently it was claimed (2) that irradiating a hydrogen peroxide solution with ultraviolet light caused the formation of a higher hydrogen peroxide, H_2O_4, but a subsequent study (*3*) showed that the phenomenon observed was caused by oxygen supersaturation. Supersaturation can be particularly troublesome in stability or kinetic studies, where rates are most easily and commonly observed by measuring the rate of oxygen evolution. A common method of surveillance of hydrogen peroxide stored in tanks is also through the oxygen evolution rate. This report summarizes the results of a quantitative study of the phenomenon (*1, 4, 6*) and provides a guide in planning and interpreting kinetic studies with hydrogen peroxide.

METHODS AND EQUIPMENT

Hydrogen peroxide undergoes a slow decomposition to water and oxygen under all conditions, even when prepared in the highest purity and stored in the most inert containers. If one starts agitating, as with a continuous stirrer, a solution which previously has been quiescent, the rate of oxygen evolution rises suddenly and then gradually drops until it returns to the original rate which represents the true H_2O_2 decomposition rate (*BCD* or *FGH*, Figure 1). If agitation is stopped, the oxygen evolution rate drops and then slowly rises to the steady-state rate (*DEF*). The area under the curve *BCD* or *FGH* above a horizontal line through *A*, *B*, *D*, *F*, and *H* represents the amount of oxygen supersaturated in the solution. (The area *DEF* below the horizontal line is another measure of the amount of supersaturation, but since a longer time is required to reach steady state after cessation of agitation, this is a less accurate method of measurement.) In ordinary laboratory glass apparatus, agitation by conventional stirrers at rotation rates of a few hundred revolutions per minute or more completely desupersaturates a hydrogen peroxide solution. Although more vigorous agitation increases the height of the curve and its steepness, the area under the curve remains the same. The oxygen supersaturation here differs from the usual gas supersaturation phenomenon in that the amount of supersaturation is essentially independent of time, being