VOLUMETRIC BEHAVIOR IN SEVERAL GASEOUS HYDROCARBON SOLUTIONS[1]

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The recent marked accumulation of information concerning the volumetric behavior of hydrocarbons and their mixtures has made it interesting to compare the various methods of prediction of such behavior with the experimental data.

A comparison has been made of volumetric data for the binary mixtures of methane with ethane, propane, and *n*-butane with predictions based on an equation of state for the mixtures. The comparison has been carried out at pressures up to 204 atm. and at temperatures from 38° to 121°C. The results indicate that for regions of low density some of the available methods are adequate for most technical uses. However, at the higher densities corresponding to the higher pressures there still remains the need for additional refinement to permit the use of equations of state in many industrial requirements.

Gaseous solutions are typified in nature by the atmosphere and by natural gas at relatively low pressures. The assumptions of the additivity of volume (18) and of the perfect gas laws can be used to approximate their behavior roughly. The additive volume concept, which is equivalent in part to the assumption of ideal solutions (17), appears to be applicable at reduced temperatures below about two only for low reduced pressures, but at high reduced temperatures for a fair range of reduced pressures. Efforts to correlate the volumetric and phase behavior of mixtures of paraffin hydrocarbons by graphical, tabular, or nomographic means have been notable for their lack of success except for the volumetric generalization proposed by Kay (16) that has come to be known as the "pseudo-critical correlation." This generalization has proven to be most useful for many purposes but is not sufficiently precise to satisfy all requirements nor does it permit direct estimation of phase behavior. These limitations in the relatively simple methods of estimation of the volumetric behavior of gaseous mixtures from a knowledge of the behavior of the components have made necessary the experimental investigation of the behavior of such phases. The work on the volumetric behavior of hydrogen and nitrogen (3, 4, 26) and of air (2, 15) has been supplemented recently by studies of natural gases (20, 25) and of a number of binary mixtures of the paraffin hydrocarbons (10, 20, 21, 22, 24). Some of these data have been employed in the evaluation of the partial volumetric behavior of these hydrocarbons in binary mixtures (23). Such information has been used for the prediction of the compressibility factor of natural gases. Most of the experimental data accumulated serve to indicate that

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gaseous solutions at elevated pressures deviate materially from the additive volume relationships, especially at low reduced temperatures.

The Beattie–Bridgeman equation (6) has been proposed for application to gaseous mixtures. Values of each coefficient, as applicable to the mixture in the single-phase region, have been taken as derivable from the corresponding coefficients for the pure components. On this basis, which was originally proposed by Beattie (5), the several coefficients of the Beattie–Bridgeman equation may be established by application of the following types of expressions:

$$A_{0_m} = \left(\sum_{i=1}^{n} n_i A_{0_i}^{1/2}\right)^2$$

$$B_{0_m} = \left(\sum_{i=1}^{n} n_i B_{0_i}\right)$$

where n_i refers to the mole fraction of the i^{th} component in the mixture.

It has been found that this method of evaluating the coefficients of the Beattie–Bridgeman equation does not yield satisfactory results insofar as the prediction of the volumetric behavior of binary and more complex hydrocarbon mixtures in the gaseous region is concerned. However, some improvements in the evaluation of the coefficients have been suggested (9). Furthermore, the Beattie–Bridgeman equation is not suitable for use at high specific weights. For example, one of the originators has indicated a value of about 4 gram-moles per liter (8) as the limiting density at which the equation is applicable to *n*-butane. This figure in the case of methane is about 6 gram-moles per liter (7).

In order to overcome the lack of applicability of the Beattie–Bridgeman equation to mixtures in the gaseous region and to materials having high specific weight, Benedict proposed (11, 12) a more complex but nevertheless more accurate expression for the estimation of the volumetric behavior of hydrocarbon mixtures. The expression proposed by Benedict appears to be of sufficient accuracy to permit its use to predict the chemical potential of the components in each of the phases. From such knowledge, the composition of the coexisting phases as a function of temperature and pressure may be estimated. These methods appear feasible of extension to practical engineering use in the estimation of the volumetric and phase behavior of multicomponent hydrocarbon systems.

The extension of such methods to the design of process equipment has been limited by the lack of specific information concerning appropriate values of the coefficients for the components of greater molecular weight than *n*-butane. Furthermore, the numerical effort associated with the establishment of the composition of the coexisting phases is significant. In the past, this effort prevented the widespread utilization of equations of state for the prediction of the composition of coexisting phases in heterogeneous, multicomponent systems. Recently, with the advent of more effective mechanical or electronic computing devices (see, for example, articles by Aiken (1) and Brainerd (13)), it appears more feasible to solve the requisite simultaneous equations by trial than in the past. Therefore it is believed that the extension of the knowledge of the co-

TABLE 1

Ratio of volumes in the methane–ethane system*

A. Temperature = 37.8°C. (100°F.)

COMPOSITION	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
MOLE FRACTION METHANE	Liter/gram-mole	Cu. ft./lb. mole	
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	0.743	11.90	0.9909
0.1	0.763	12.23	0.9981
0.2	0.783	12.55	1.0015
0.4	0.821	13.15	1.0024
0.6	0.851	13.63	1.0034
0.8	0.875	14.02	1.0045
1.0	0.900	14.41	0.9998
Pressure = 68.05 atm. (1000 lb./sq. in.)			
0.0	0.0964	1.544	0.9954
0.1	0.1410	2.259	0.92†
0.2	0.1828	2.928	1.0058
0.4	0.2485	3.98	1.0064
0.6	0.2890	4.63	1.0045
0.8	0.317	5.08	1.0049
1.0	0.340	5.45	0.9984
Pressure = 204.1 atm. (3000 lb./sq. in.)			
0.0	0.0742	1.189	0.9978
0.1	0.0750	1.202	0.9940
0.2	0.0760	1.217	0.9954
0.4	0.0788	1.262	1.0084
0.6	0.0841	1.347	1.0303
0.8	0.0932	1.493	1.0285
1.0	0.1069	1.713	1.0025

B. Temperature = 121.1°C. (250°F.)

COMPOSITION	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
MOLE FRACTION METHANE	Liter/gram-mole	Cu. ft./lb. mole	
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	1.087	17.41	0.9979
0.2	1.106	17.71	1.0032
0.4	1.124	18.00	1.0037
0.6	1.142	18.29	1.0029
0.8	1.158	18.55	1.0013
1.0	1.173	18.79	0.9985

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* Ratio of volume calculated from Benedict equation to experimental volume.

† Value omitted from figure. Curve dotted in the vicinity because exact shape not established.

TABLE 1—*Concluded*

B. Temperature = 121.1°C. (250F.°)—*Concluded*

COMPOSITION	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
MOLE FRACTION METHANE	Liter/gram-mole	Cu. ft./lb. mole	
	Pressure = 68.05 atm. (1000 lb./sq. in.)		
0.0	0.373	5.97	0.9912
0.2	0.395	6.32	1.0132
0.4	0.414	6.63	1.0091
0.6	0.431	6.91	1.0087
0.8	0.447	7.16	1.0065
1.0	0.463	7.41	0.9966
	Pressure = 204.1 atm. (3000 lb./sq. in.)		
0.0	0.1089	1.745	0.9951
0.2	0.1174	1.881	1.06†
0.4	0.1261	2.020	1 0173
0.6	0.1352	2.165	1.0235
0.8	0.1446	2.317	1.0172
1.0	0.1546	2.476	1.0008

efficients for the Benedict equation to the paraffinic hydrocarbons of higher molecular weight will be worth while. With the completion of the study of the behavior of binary and ternary systems of olefinic and paraffinic hydrocarbons, it will be possible to develop a sufficient background of information to permit the prediction of the behavior of multicomponent hydrocarbon systems of low and intermediate molecular weight. Such calculations should be capable of accomplishment with the accuracy necessary for nearly any engineering application.

It is the purpose of the present discussion to review the accuracy with which the volumetric behavior of several binary paraffin hydrocarbon systems may be predicted from the available constants for the Benedict equation of state (11, 12). Since no constants for the Benedict equation for paraffin hydrocarbons of higher molecular weight than *n*-butane are available, it has been necessary to limit the systems which may be included in the comparison. In table 1 are presented the values of the ratio of molal volumes estimated from the Benedict equation with those obtained from experimental measurements (22) for the methane–ethane system. The experimentally determined molal volumes have been included in this tabulation. The range of pressures and temperatures includes the greater part of states covered by the experimental investigation. The volume ratios for this system are portrayed graphically in figures 1 and 2. In the figures, dotted lines indicate that the volume ratios have not been established in sufficient detail in the regions indicated to draw the correct curves. If the experimental points in these regions are not in the range of the graph, they are omitted. The agreement between the predicted and experimental values is, for the most part, better for the pure substances than for mixtures, but is reasonably good at nearly all states. It is understood that the data for the methane–ethane system (22) were not employed in the derivation of the

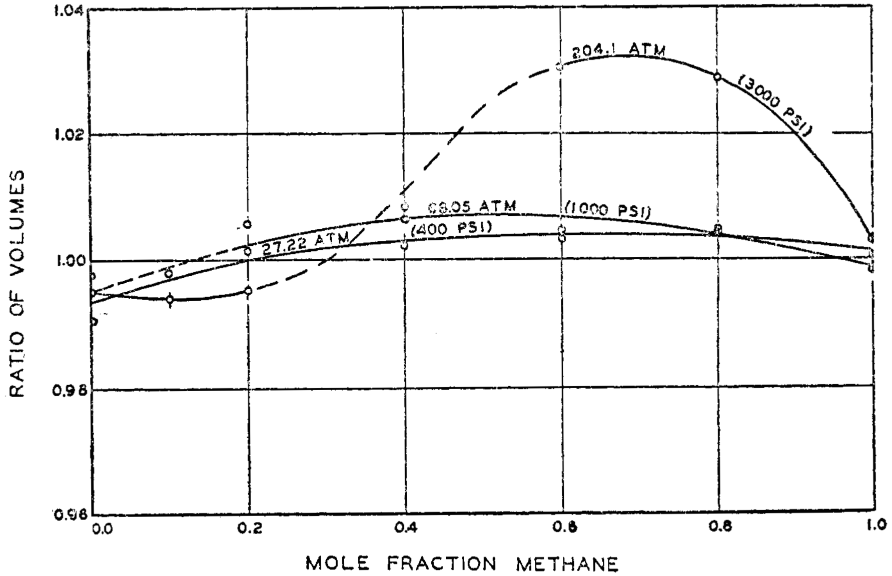

FIG. 1. Ratio of volumes for the methane–ethane system at 37.8°C. (100°F.)

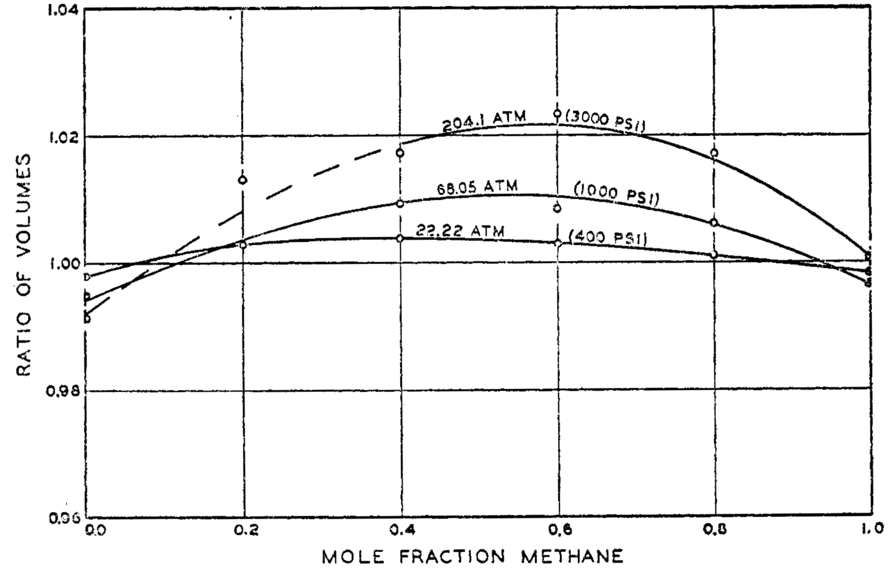

FIG. 2. Ratio of volumes for the methane–ethane system at 121.1°C. (250°F.)

constants for methane and ethane in the Benedict equation (11, 12). The standard deviation of the predicted values from the experimental measurements

TABLE 2

Ratio of volumes in methane–propane system*

Temperature = 37.8°C. (100°F.)

COMPOSITION MOLE FRACTION METHANE	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
	Liter/gram-mole	Cu. ft./lb. mole	
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	0.0923	1.479	1.021
0.0845†			
0.4419‡			
0.6	0.783	12.55	1.025
0.7	0.823	13.19	1.0086
0.8	0.854	13.68	1.0057
1.0	0.900	14.41	0.9998
Pressure = 68.05 atm. (1000 lb./sq. in.)			
0.0	0.0900	1.441	1.0216
0.2	0.0889	1.424	1.0176
0.3	0.0926	1.484	0.9998
0.3271†			
0.6635‡			
0.7	0.2653	4.25	0.9934
0.8	0.2947	4.72	1.0070
1.0	0.340	5.45	0.9984
Pressure = 204.1 atm. (3000 lb./sq. in.)			
0.0	0.0848	1.358	1.0280
0.2	0.0803	1.287	1.0310
0.3	0.0790	1.266	1.0283
0.6	0.0813	1.302	0.9978
0.7	0.0854	1.368	0.9905
0.8	0.0914	1.464	0.9898
1.0	0.1069	1.713	1.0025

* Ratio of volume calculated from Benedict equation to experimental volume.

† Bubble-point composition.

‡ Dew-point composition.

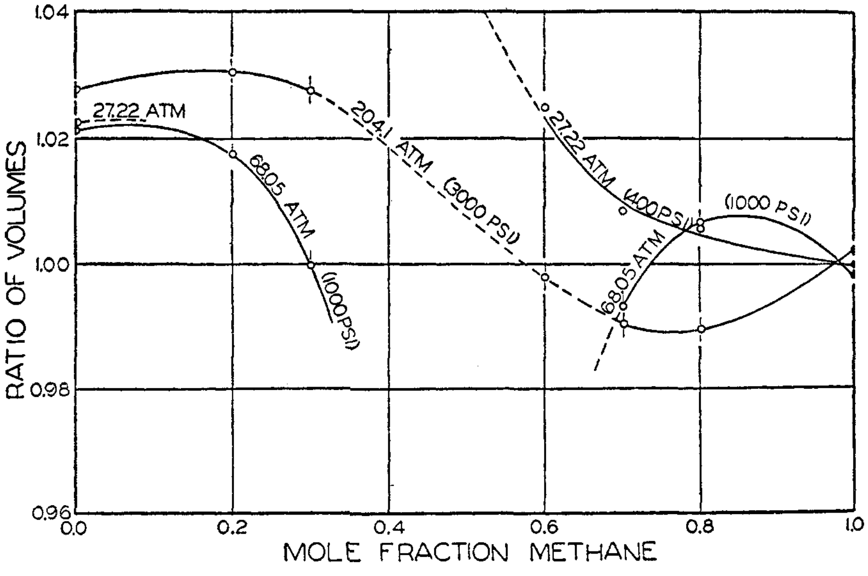

FIG. 3. Ratio of volumes for the methane–propane system at 37.8°C. (100°F.)

TABLE 3

Ratio of volumes in the methane-n-butane system*

A. Temperature = 37.8°C. (100°F.)

COMPOSITION MOLE FRACTION METHANE	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
	Liter/gram-mole	Cu. ft./lb. mole	
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	0.1033	1.655	1.0129
0.1208†			
0.8221‡			
0.9	0.860	13.77	1.0136
0.1	0.900	14.41	0.9998
Pressure = 68.05 atm. (1000 lb./sq. in.)			
0.0	0.1019	1.632	1.0157
0.2	0.0943	1.511	1.0216
0.3	0.0918	1.471	1.0192
0.3172†			
0.8818‡			
0.9	0.312	4.99	0.9974
1.0	0.340	5.45	0.9984
Pressure = 204.1 atm. (3000 lb./sq. in.)			
0.0	0.0984	1.577	1.0204
0.2	0.0895	1.434	1.032
0.3	0.0860	1.378	1.0288
0.6	0.0809	1.296	1.0054
0.8	0.0851	1.364	1.0085
0.9	0.0938	1.503	1.0131
1.0	0.1069	1.713	1.0025

B. Temperature = 121.1°C. (250°F.)

COMPOSITION MOLE FRACTION METHANE	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
	Liter/gram-mole	Cu. ft./lb. mole	
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	0.1358	2.175	0.9952
0.0216†			
0.1417‡			
0.2	0.779	12.48	1.09§
0.4	0.938	15.02	1.0534
0.6	1.039	16.65	1.0350
0.8	1.111	17.80	1.0215
1.0	1.173	18.79	0.9985

* Ratio of volume calculated from Benedict equation to experimental volume.

† Bubble-point composition.

‡ Dew-point composition.

§ Value omitted from figure.

TABLE 3—*Concluded*

B. Temperature = 121.1°C. (250°F.)—*Concluded*

COMPOSITION	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
MOLE FRACTION METHANE	Liter/gram-mole	Cu. ft./lb. mole	
Pressure = 68.05 atm. (1000 lb./sq. in.)			
0.0	0.1262	2.021	1.0033
0.2	0.1405	2.250	0.9780
0.2192†			
0.4326‡			
0.6	0.358	5.74	1.0192
0.8	0.416	6.66	1.0220
1.0	0.463	7.41	0.9966
Pressure = 204.1 atm. (3000 lb./sq. in.)			
0.0	0.1140	1.826	1.0138
0.2	0.1075	1.722	1.0203
0.4	0.1057	1.693	1.0228
0.6	0.1144	1.832	1.0220
0.8	0.1333	2.135	1.0182
1.0	0.1546	2.476	1.0008

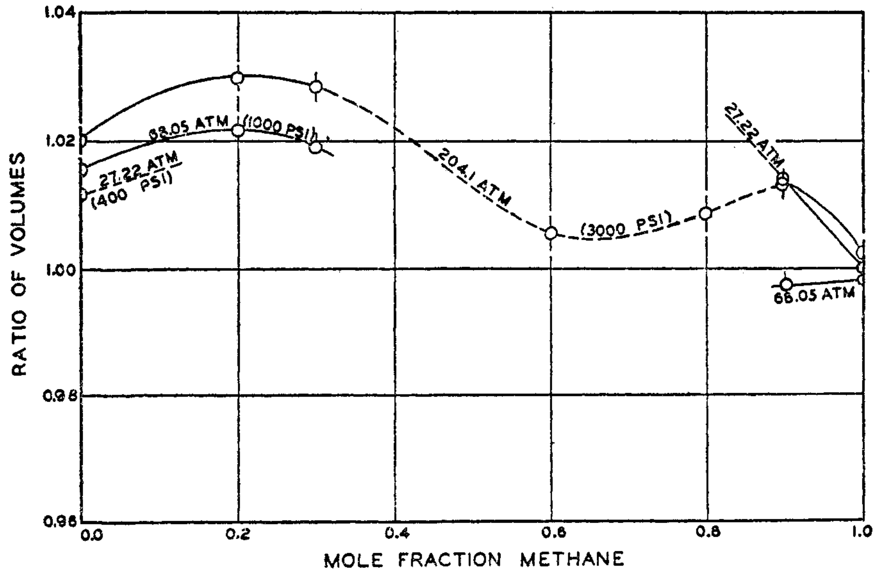

FIG. 4. Ratio of volumes for the methane-*n*-butane system at 37.8°C. (100°F.)

for the methane–ethane system is about 0.2 per cent for the curve at 27.22 atm. (400 lb./sq. in.) and 121.1°C. (250°F.) and about 2 per cent for the curve at 204.1 atm. (3000 lb./sq. in) and 37.8°C. (100°F.).

A comparison of the ratio of estimated to experimental molal volumes for the

TABLE 4

Ratio of volumes in the methane–ethane system for ideal solutions*

A. Temperature = 37.8°C. (100°F.)

COMPOSITION MOLE FRACTION METHANE	EXPERIMENTAL VOLUME Liter/gram-mole	EXPERIMENTAL VOLUME Cu. ft./lb. mole	RATIO OF VOLUMES*
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	0.743	11.90	1.0000
0.2	0.783	12.55	0.9882
0.4	0.821	13.15	0.9810
0.6	0.851	13.63	0.9836
0.8	0.875	14.02	0.9922
1.0	0.900	14.41	1.0000
Pressure = 68.05 atm. (1000 lb./sq. in.)			
0.0	0.0964	1.544	1.0000
0.2	0.1828	2.928	0.7941
0.4	0.2485	3.98	0.7800
0.6	0.2890	4.63	0.8397
0.8	0.317	5.08	0.9198
1.0	0.340	5.45	1.0000
Pressure = 204.1 atm. (3000 lb./sq. in..)			
0.0	0.0742	1.189	1.0000
0.2	0.0760	1.217	1.0635
0.4	0.0788	1.262	1.1084
0.6	0.0841	1.347	1.1161
0.8	0.0932	1.493	1.0773
1.0	0.1069	1.713	1.0000

B. Temperature = 121.1°C. (250°F.)

COMPOSITION MOLE FRACTION METHANE	EXPERIMENTAL VOLUME Liter/gram-mole	EXPERIMENTAL VOLUME Cu. ft./lb. mole	RATIO OF VOLUMES*
Pressure = 27.22 atm. (400 lb./sq. in.)			
0.0	1.087	17.41	1.0000
0.2	1.106	17.71	0.9990
0.4	1.124	18.00	0.9977
0.6	1.142	18.29	0.9975
0.8	1.158	18.55	0.9977
1.0	1.173	18.79	1.0000

* Ratio of volume calculated on the assumption of an ideal solution to experimental volume.

TABLE 4—*Concluded*

B. Temperature = 121.1°C. (250°F.)—*Concluded*

COMPOSITION MOLE FRACTION METHANE	EXPERIMENTAL VOLUME		RATIO OF VOLUMES*
	Liter/gram mole	Cu. ft./lb. mole	
Pressure = 68.05 atm. (1000 lb./sq. in.)			
0.0	0.373	5.97	1.0000
0.2	0.395	6.32	0.9908
0.4	0.414	6.63	0.9878
0.6	0.431	6.91	0.9881
0.8	0.447	7.16	0.9946
1.0	0.463	7.41	1.0000
Pressure = 204.1 atm. (3000 lb./sq. in.)			
0.0	0.1089	1.745	1.0000
0.2	0.1174	1.881	1.0055
0.4	0.1261	2.020	1.0082
0.6	0.1352	2.165	1.0089
0.8	0.1446	2.317	1.0054
1.0	0.1546	2.476	1.0000

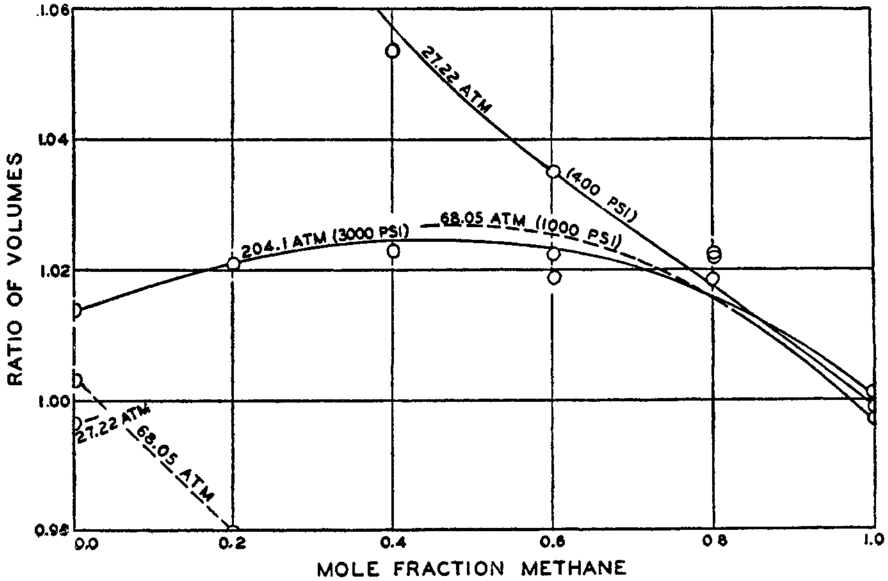

FIG. 5. Ratio of volumes for the methane–*n*-butane system at 121.1°C. (250°F.)

methane–propane system is given in table 2 and figure 3. Similar data for the methane–*n*-butane system are given in table 3 and figures 4 and 5. Fairly satisfactory agreement between the estimated and experimental values was obtained even though in some instances the system was in the liquid phase. In the figures

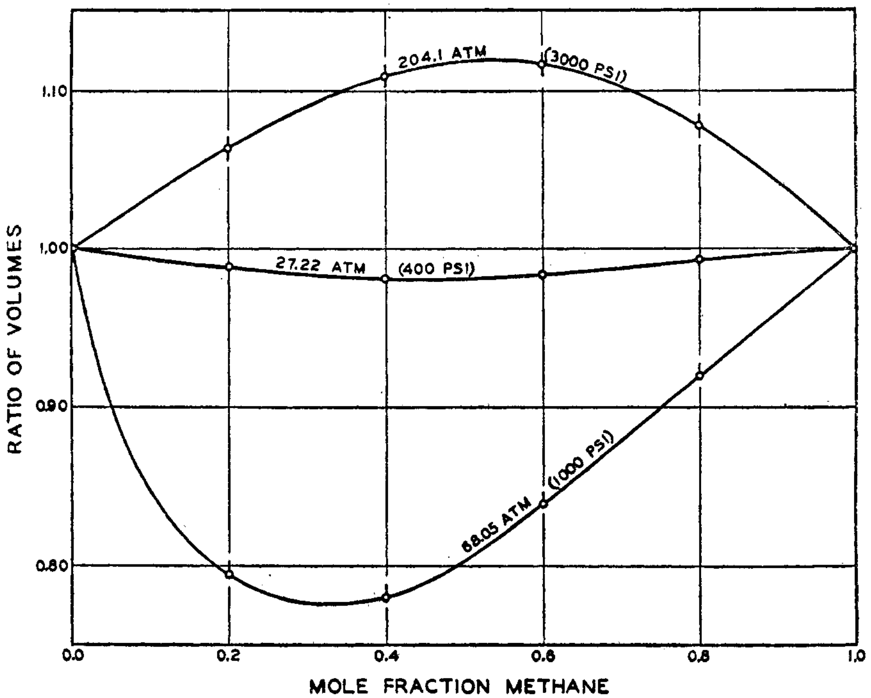

FIG. 6. Ratio of volumes for ideal solution in the methane-ethane system at 37.8°C. (100°F.)

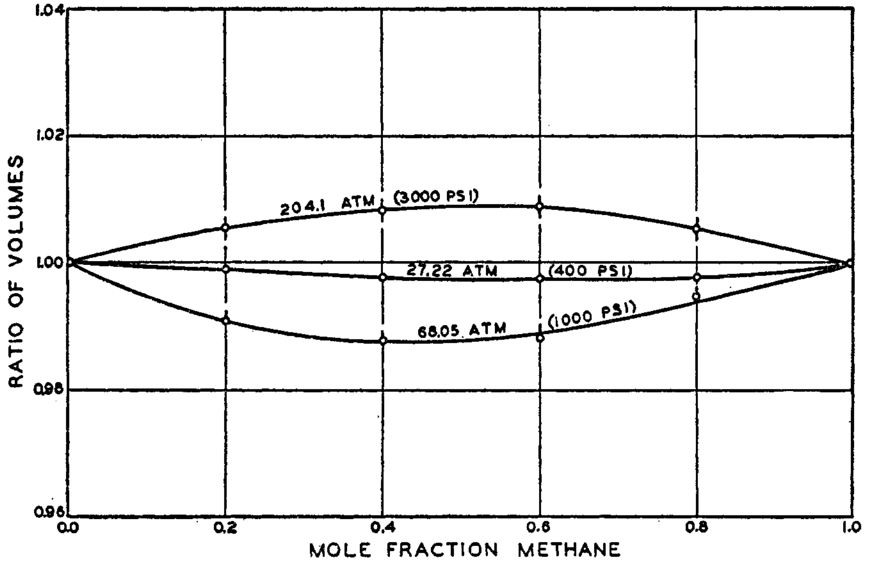

FIG. 7. Ratio of volumes for ideal solution in the methane-ethane system at 121.1°C. (250°F.)

the end of a curve within the boundaries of the graph indicates the presence of a bubble- or a dew-point. As a matter of interest the corresponding experimentally determined molal volumes have been included in the tables along with the bubble-point and dew-point compositions when heterogeneous equilibrium was involved. It is surprising that larger deviations between the predicted and experimental data do not exist at the higher pressures. The assumptions (14) often made in regard to the contribution of the components of a gaseous mixture to the behavior of the system are not applicable at the higher pressures.

A prediction of the volume of one system is made on assumptions of ideal solution because of the use of the method in the process industries. The data for mixtures of methane and ethane are presented in table 4 and in figures 6 and 7. Satisfactory agreement is obtained at lower pressures.

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