Supersaturation in Hydrocarbon Systems Methane–n-Decane

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A review of some of the experimental work associated with the supersaturation of hydrocarbon liquids has been made available recently *(8)*. Kennedy and Olson *(5)* found it possible to maintain hydrocarbon liquids at pressures markedly below bubble point for short time intervals. In order to extend the data in this field a study of the supersaturation in hydrocarbon liquids was undertaken.

The molecular theory of liquids *(1,2,6,7)* indicates that significant local fluctuations in the state variables are to be expected at a point as a function of time. These fluctuations result in a wide variation in the time during which a system will remain in a strained condition at an invariant macroscopic state. Measurements of the time that four mixtures of methane and *n*-decane could be maintained under different conditions of strain were determined for each of three temperatures. Since the time of strain appears to be random in time *(4,8)*, numerous measurements at each condition were required in order to establish the behavior. The standard deviation of the time of strain approaches the mean value as the number of measurements is increased. A regression analysis *(8)* was made of the experimental information obtained under each condition of strain for each of the four mixtures. A review of the statistical analysis is available *(4,8)*. The term "strain" as here used implies the displacement of the dependent variable of interest from its equilibrium value at the state in question.

MATERIALS

Methane used in this investigation was obtained from the San Joaquin Valley of California. As received at the laboratory it contained approximately 0.0001 mole fraction carbon dioxide, 0.0007 mole fraction propane, and 0.0012 mole fraction ethane. The gas was in equilibrium in an aqueous phase at a pressure of approximately 1400 p.s.i. The nearly pure methane was passed over calcium chloride, activated charcoal, potassium hydroxide, and anhydrous calcium sulfate at a pressure in excess of 500 p.s.i. It was passed through a trap at the temperature of solid carbon dioxide and warmed to room temperature before being used. The gas employed did not contain more than 0.002 mole fraction of material other than methane, as established by mass spectrographic analysis.

The *n*-decane was obtained from Matheson Coleman and Bell. It was used for these measurements after fractionation at low pressure in a column with 30 plates and deaeration and drying by prolonged refluxing in contact with sodium at reduced pressure. A specific weight at atmospheric pressure of 45.339 pounds per cubic foot at 77° F. was found for the deaerated sample as compared to a value of 45.337 pounds per cubic foot at a temperature of 77° F. reported by Rossini *(9)*. An index of refraction at 77° F. of 1.40974 was obtained for the *D*-lines of sodium as compared to a value of 1.40967 reported by Rossini *(9)* for an air-saturated sample.

METHODS AND EQUIPMENT

The method employed in this investigation involved maintaining one relatively small portion of the system at a somewhat higher temperature than the remainder, thus localizing the region in which supersaturation occurred. The portion of the system at the higher temperature was in a strained condition while the remainder at the lower temperature was maintained at a pressure above bubble point. Such an arrangement permitted the configuration of the system subjected to strain to be relatively simple, without the existence of liquid-liquid interfaces, packing glands, and other devices which might have a significant influence upon the time-strain relationships of the system. The details of the equipment have been described *(8)*.

The mixtures were prepared by the introduction of the desired amounts of *n*-decane and methane by high-vacuum techniques. The equilibrium bubble-point pressure was determined for the temperature of interest. A given mixture was often used over a period of months and it was found that the standard deviation of the bubble-point pressures measured at different times at the same temperature was not more than 0.45 p.s.i.

The fluid was brought to physical equilibrium at the desired temperature and was maintained at a pressure of 1000 p.s.i. above bubble point for a specified period of time, usually several hours. Variations in the time of agitation and of conditioning at a pressure markedly in excess of bubble point were investigated with one mixture and not found to exert any statistically significant effect on the time of strain. The temperature of a portion of the fluid, having a volume of 0.000411 cubic foot and a surface area of 0.0567 square foot, was raised a predetermined amount in order to bring the bubble-point pressure of this part of the fluid above that of the main body. The pressure was then slowly reduced by withdrawal of mercury to a value just above the bubble-point pressure of the main body of liquid. The portion of the system at the higher temperature was thus maintained at a pressure below the equilibrium bubble point for the mixture. The formation of a bubble was indicated by the requirement for an increase in the total volume of the system in order to maintain isobaric conditions. Such methods are suitable only for mixtures for which the equilibrium bubble-point pressure increases with an increase in temperature.

EXPERIMENTAL RESULTS

Typical results for a mixture of methane and *n*-decane containing 0.0355 mole fraction methane at a stress of 29.68 p.s.i. are shown in Figure 1. The bubble-point pressure at equilibrium for 160° F. was 120 p.s.i. The sample was maintained under nearly isobaric-isothermal conditions throughout the period of strain. The times of strain for a particular set of conditions of stress were obtained from a series of experimental measurements such as the one depicted in Figure 1. A summary of the experimental results obtained with four mixtures at temperatures ranging from 70° to 390° F. is recorded in Table I. The deviation from isobaric conditions of strain was sufficiently small, as indicated by the standard deviations in pressure, that only minor corrections in time of strain were made *(8)* to account for the small changes in pressure with time. During the period when these measurements were made it was not feasible to hold the temperature of the system at systematically chosen values, which would have been desirable.

Utilizing the data of Table I, there is shown in Figure 2 for a mixture containing 0.2765 mole fraction methane the probability of a bubble not being formed under one experimental condition of strain as a function of time. The volume, area, and temperature indicated refer only to that portion of the system under strain. The mixture had an equilibrium bubble-point pressure of 1048 p.s.i. and was

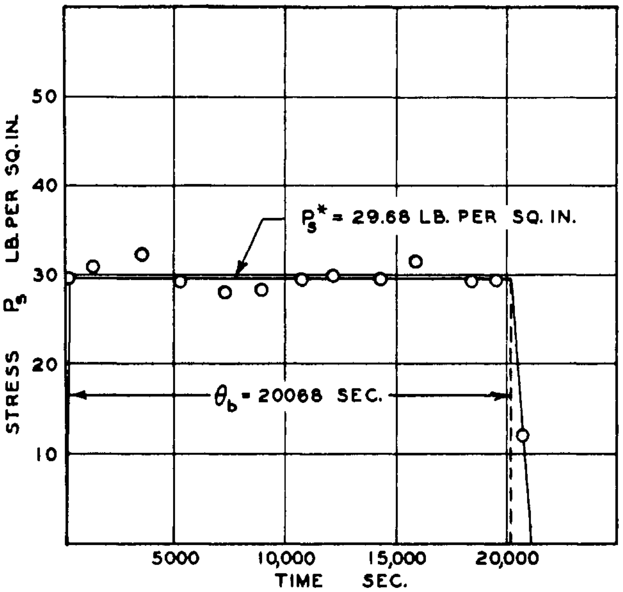

Figure 1. Typical experimental results for a mixture containing 0.0355 mole fraction methane

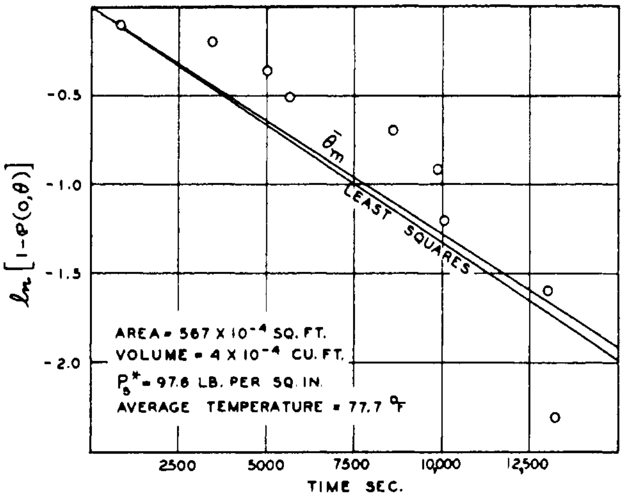

Figure 2. Probability of a bubble not being formed in a mixture containing 0.2765 mole fraction methane

subjected to a stress of approximately 97.6 p.s.i. The primary variable, $P(0, \theta)$, of the ordinate of Figure 2 was determined from the difference between unity and the ratio of the number of trials with supersaturation times less than that of, but including, the trial in question to the total number of trials plus one *(3)*. A straight line *(4)* was fitted to the data of Figure 2 by the method of least squares. The slope of this line would be identical with the mean time for the formation of the first bubble *(8)* if a sufficiently large number of trials were made and if the physical phenomena were truly random in time. The slope of such a line for each of the conditions of supersaturation investigated is included in Table II. The value of the slope computed from mean time is also recorded along with the standard deviation of the times of strain from the mean time. These data indicate, within the error of measurement, that the formation of a bubble in a fixed total volume is random with respect to time *(10)* as was predicted from the theory of liquids *(2, 6, 7)* and found experimentally for pure propane *(4)* and pure *n*-pentane *(8)*.

The time of strain is shown in Figure 3 as a function of the supersaturation pressure for the same mixture of 0.2765 mole fraction methane. Again the volume, area, and temperature refer only to that portion of the system under strain. There is a decrease in the time of strain with an increase in supersaturation pressure. This trend is apparent despite more than a tenfold variation in time of strain at a fixed supersaturation pressure. The same information is presented in Figure 4 except that it has been assumed that the Arrhenius relation describes the effect of supersaturation upon time of strain *(4, 8)*. The curve drawn on Figure 3 is represented by a second degree equation fitted to the data by least squares methods. The straight line of Figure 4 was fitted by a regression analysis. It was assumed that the formation of bubbles is randomly distributed in time, thus resulting in a Poisson's distribution function. The assumption of this form of distribution leads to a linear relationship between the logarithm of the time for the for-

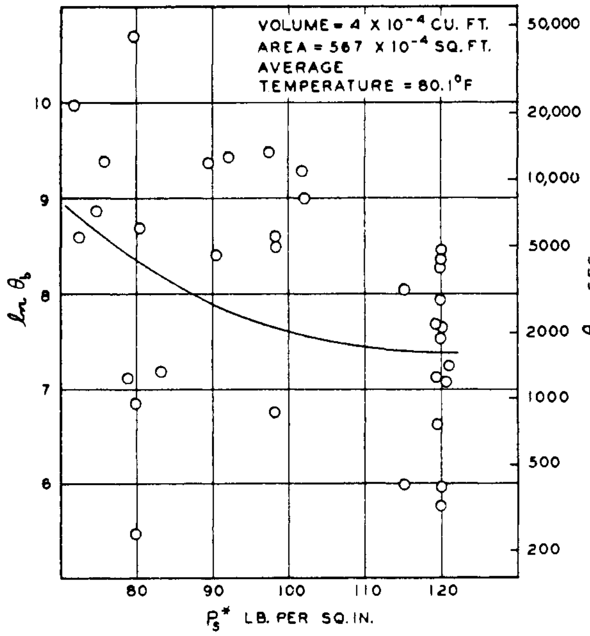

Figure 3. Effect of stress on time of strain for a mixture containing 0.2765 mole fraction methane

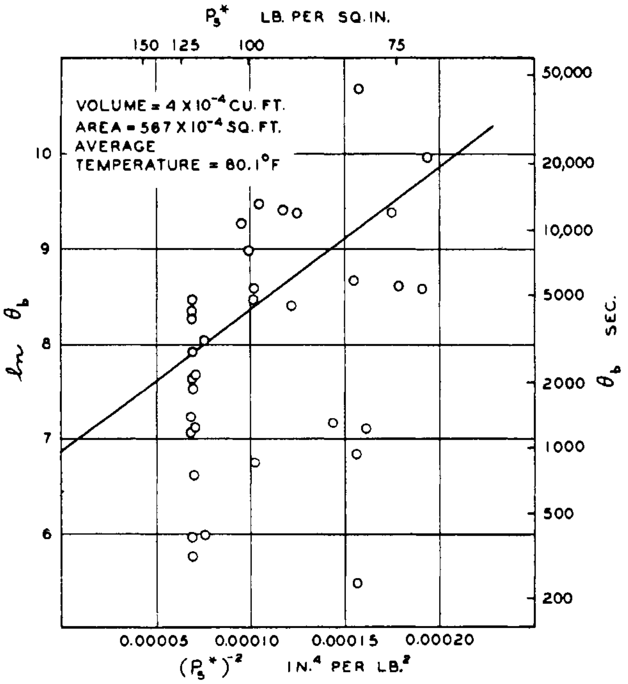

Figure 4. Application of Arrhenius relation to behavior of mixture containing 0.2765 mole fraction methane

Table I. Summary of Experimental Results for Mixtures of Methane and *n*-Decane in Heated Thimble Equipment

No. of Experimental Points	Av. Supersaturation Pressure, P.S.I.	Standard Deviation, P.S.I.	Bubble Formation Time, Sec.	Rate of Bubble Formation, Bubbles/(Sec.)(Cu. Ft.)	Thimble Temp., °F.
Mole Fraction Methane = 0.2765					
Average Thimble Temperature = 77.7°F.					
1	115.13^{a}	0	395	6.161	88.98
3	115.18	0	3,098	0.785	89.06
2	119.34	0.71	2,156	1.128	87.72
10	119.97	0.32	4,714	0.516	88.00
1	119.88	0	387	6.285	88.31
8	120.00	0.35	4,245	0.573	88.17
10	119.89	0	2,766	0.880	88.13
6	119.50	0.52	753	3.231	87.86
5	120.63	1.10	1,178	2.065	88.56
4	119.83	0	1,870	1.301	88.10
1	119.79	0	318	7.651	88.23
10	119.79	0	3,908	0.623	87.84
7	119.95	0.38	2,095	1.161	88.16
6	119.31	0.55	1,246	1.953	87.86
6	120.81	0	1,392	1.748	88.51
10	97.47	1.41	13,050	0.186	78.87
3	98.81	0	855	2.846	79.02
11	98.81	0	4,837	0.503	78.92
7	98.80	0	5,375	0.453	79.06
12	102.05	0.58	8,006	0.304	79.14
21	101.66	1.60	10,714	0.227	79.23
19	89.35	6.19	11,687	0.208	75.22
6	90.48	2.61	4,384	0.555	75.09
2	83.20	0.96	1,315	1.850	70.73
7	80.32	2.70	5,810	0.419	70.93
1	79.78	0	238	10.225	70.71
64	79.50	2.34	43,295	0.056	71.05
19	92.11	3.19	12,354	0.197	74.99
4	79.76	0	937	2.597	71.00
4	78.77	1.10	1,225	1.986	70.71
9	72.42	1.81	5,391	0.451	68.07
9	74.67	0.15	7,055	0.345	68.06
39	71.75	4.13	21,437	0.113	68.14
24	75.67	3.75	11,932	0.204	70.78
Mole Fraction Methane = 0.2325					
Average Thimble Temperature = 273.1° F.					
8	124.42^{a}	0.38	5,963	0.408	287.21
8	101.46	2.23	9,503	0.256	252.22
63	91.34	2.69	84,508	0.029	243.61
48	102.20	5.02	65,923	0.037	251.92
1	124.80	0	328	7.418	288.78
82	105.78	5.06	83,111	0.029	256.60
38	115.08	1.89	33,327	0.073	267.67
12	124.35	0.52	1,595	1.526	287.08
17	113.60	3.48	13,754	0.177	268.02
12	123.42	2.45	6,579	0.370	287.54
4	112.64	3.20	1,623	1.499	267.97
4	129.36	0.75	892	2.732	308.48
12	129.45	0.17	1,702	1.430	308.76
17	129.08	2.21	4,614	0.527	309.58
57	115.20	2.78	64,356	0.038	268.05
4	105.42	0.77	1,627	1.495	257.07
10	102.24	4.98	6,027	0.404	257.16
7	123.21	3.07	3,475	0.700	287.41
7	129.44	0.14	1,122	2.169	308.42
16	101.25	1.49	12,782	0.190	252.54
2	129.74	0	972	2.503	310.66
18	100.19	2.52	13,252	0.184	252.76
Mole Fraction Methane = 0.0120					
Average Thimble Temperature = 359.3°F.					
3	8.25^{a}	0.06	2,589	0.940	350.07
2	17.89	0.06	153	15.898	386.97
2	17.32	0.01	202	12.048	385.19
14	6.76	0.75	12,985	0.187	353.01
3	15.01	0	405	6.006	377.16
15	6.45	0.57	17,652	0.138	343.34
28	6.87	0.64	34,011	0.072	342.46
4	9.48	0.07	4,548	0.535	355.53
2	14.76	0.01	174	13.986	376.62
22	9.53	0.51	46,889	0.052	355.55
2	14.70	0.06	398	6.112	376.36
1	9.27	0	589	4.131	354.80
5	9.44	0.08	10,705	0.227	355.60
10	9.48	0.94	17,229	0.141	355.58
Mole Fraction Methane = 0.0355					
Average Thimble Temperature = 311.0°F.					
1	30.55^{a,b}	...	295	8.248	328.29
3	29.63	0.14	3,058	0.796	306.96
27	29.65	2.04	51,056	0.048	307.03
12	29.68	1.22	20,068	0.121	307.09
5	29.39	0.60	6,265	0.388	307.19
11	29.54	2.47	19,847	0.123	307.10
9	29.82	0	15,270	0.159	307.04
54	29.76	1.17	108,731	0.022	307.02
6	28.53	3.63	7,583	0.321	307.30
40	29.72	1.22	92,207	0.026	306.99
37	29.66	2.44	30,876	0.079	307.14
28	31.95	1.34	52,884	0.046	314.10
4	30.88	0.66	1,214	2.004	314.08
31	30.82	1.71	27,892	0.087	314.08
5	30.25	1.55	793	3.068	314.00
6	30.98^{c}	1.03	2,964	0.821	313.97
3	30.03	1.87	661	3.681	314.04
4	31.32	0.41	1,976	1.231	314.24
11	31.57	1.77	14,830	0.164	314.12
12	30.23	2.17	7,579	0.321	311.15
10	30.49	1.14	10,970	0.222	311.29
15	30.10	1.30	15,605	0.156	311.10
24	30.50	1.90	23,059	0.106	311.04
11	31.29	1.26	7,441	0.327	310.93
10	30.24	1.42	7,373	0.330	310.94
6	30.88	0.62	3,366	0.723	311.13
20	31.01	1.92	19,670	0.124	310.99
9	28.93	3.90	5,459	0.446	311.14
8	28.88	2.94	3,509	0.693	311.23
8	28.89	2.21	2,443	0.996	310.97
8	30.24	1.53	5,223	0.466	311.06
18	30.42	0.29	19,965	0.122	311.08
7	28.69	3.21	4,498	0.541	311.19
3	29.22	1.86	565	4.306	310.79
52	30.33	1.70	56,030	0.043	310.07
46	31.27	1.14	77,199	0.032	311.07
39	31.62	0.71	67,059	0.036	311.16
37	30.48^{d}	1.53	39,541	0.062	311.43
2	29.90	1.19	1,098	2.216	311.00
5	30.69	0.41	5,361	0.454	311.25
25	29.96	1.24	39,487	0.062	311.09
40	31.36	0.65	63,397	0.038	311.03
2	30.42	0.71	2,089	1.165	311.12
39	31.26	0.89	56,700	0.043	311.01

[a] Average supersaturation pressure.
[b] 10-minute agitation time.
[c] 25-minute agitation time.
[d] 100-minute agitation time.

mation of a bubble and the reciprocal of the square of the supersaturation pressure. The appropriate value of the slope must be established by a trial and error solution of the equation resulting from a conventional regression analysis of the Poisson's distribution assuming the Arrhenius relationship for the rate of formation of bubbles. The standard deviation in time for the data shown was 8311 seconds for Figure 3 and 7548 seconds in Figure 4.

Utilizing the data of Table II and assuming Poisson distribution, the probability of a bubble forming *(8)* as a function of time for a given degree of strain is shown in Figures 5 and 6 for a total volume of liquid phase of 0.000411

Table II. Comparison of Predicted and Experimental Standard Deviations

Av. Thimble Temp., °F.	Compn. Mole Fraction Methane	No. of Measurements	Supersaturation Pressure, P.S.I.	Mean Time to First Bubble, Sec.		Rate of Bubble Formation, Bubbles/(Sec.) (Cu. Ft.)	
				Exptl.	Std. dev.^{a}	Exptl.	Least squares
88.2	0.2765	15	119.5^b	2,017	1,430	1.206	1.319
77.7	0.2765	9	97.59	7,787	4,274	0.312	0.341
70.0	0.2765	10	77.85	9,164	14,036	0.265	0.411
298.4	0.2325	10	127.0	2,509	1,942	0.971	0.988
267.9	0.2325	4	112.5	26,696	23,632	0.091	0.110
253.0	0.2325	8	101.5	32,431	43,351	0.075	0.096
380.5	0.0120	5	15.62	263	95	9.246	9.903
354.5	0.0120	6	9.21	16,097	21,537	0.151	0.235
342.9	0.0120	3	6.67	25,128	19,924	0.097	0.139
310.4	0.0355	15	29.99^c	29,179	33,571	0.083	0.093
311.6	0.0355	22	30.32^d	16,247	21,794	0.149	0.117
311.1	0.0355	7	30.58^e	29,750	26,552	0.082	0.070

[a] Deviation from mean time.
[b] Reference supersaturation pressure.
[c] 10-minute agitation time.
[d] 25-minute agitation time.
[e] 100-minute agitation time.

cubic foot. The confidence limits of the data set forth in Table II are rather poor, since only a small number of trials at each state were made. The low confidence limit results from the statistical nature of the phenomenon and not from the uncertainties in the measurements. Wide disagreements from the predictions are to be encountered for a particular trial. A comparison of the mean time to the first bubble is given in Table II. The experimental value was obtained directly from the data of Table I while the standard deviation of the data for the trial made should approach the experimental value as the number of trials is increased without limit (*4,8*). In a similar fashion, a comparison of the rates of bubble formation (*4,8*) has been included. In Figure 5, for a mixture containing 0.0120 mole fraction methane at 354.5° F., a probability of bubble formation of 0.71 at 20,000 seconds at a stress of 9.21 p.s.i. is indicated. As shown in Figure 6, a stress of 112.5 pounds per square inch may be realized with an equal probability of bubble formation for nearly 35,000 seconds in the case of a mixture containing 0.2325 mole fraction methane at 267.9° F.

In order to present some of the trends of the data, the probability of bubble formation is shown in Figure 7 for tnree rather widely different conditions. Within the confidence limits of the data the probability of bubble formation at a given time is not greatly different for the three conditions. It is of interest to note the much higher degree of supersaturation that can be obtained at the higher weight fractions of methane with substantially the same probability of bubble formation. The data also indicate a trend to higher supersaturation pressure for the same probability of bubble formation with an increase in temperature at fixed composition.

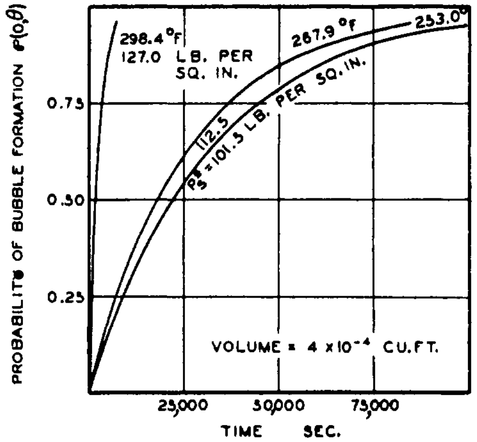

Figure 6. Probability of bubble formation for a mixture containing 0.2325 mole fraction methane

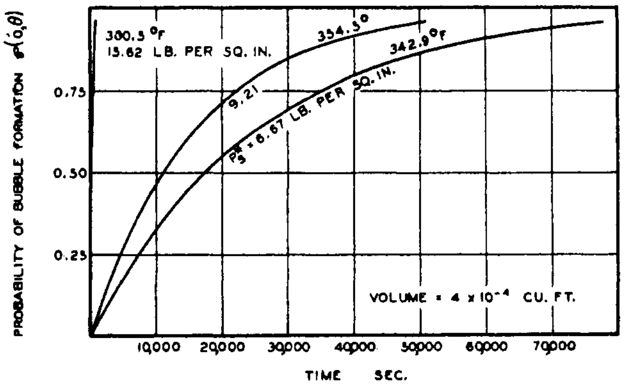

Figure 5. Probability of bubble formation for a mixture containing 0.0120 mole fraction methane

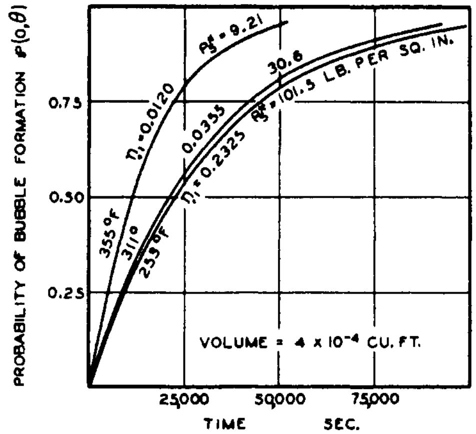

Figure 7. Trends in probability of bubble formation

ACKNOWLEDGMENT

L. T. Carmichael contributed to the experimental program and Virginia Berry aided in the preparation of the results in a form suitable for publication. W. N. Lacey reviewed the manuscript.

NOMENCLATURE

ln = natural logarithm
n_1 = mole fraction methane
P = pressure, lb./sq. inch
$\mathcal{P}$ = probability of a bubble being formed
P_b = bubble point pressure, lb./sq. inch
P_s = supersaturation pressure $(P_b - P)$, lb./sq. inch
θ = time, sec.
θ_b = time of strain to first bubble, sec.
θ_m = mean time corresponding to a given value of supersaturation pressure, sec.

SUPERSCRIPT

* = time average of quantity during run

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P-V-T and Related Properties for Methane and Ethane

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The American Petroleum Institute Research Project 44 (*19*) began to work in 1952 on the collection and critical analysis and correlation of the existing data on the *P-V-T* and related properties for the simple hydrocarbons, with the aim of providing tables of selected values of these properties. The work has now reached the stage where the first tables of the series, on methane and ethane, are appearing. The first report (*7*) described the general plan of the work, the properties for which values are tabulated, the general procedure for analysis, correlation, and calculation of the data, and the tables produced and contemplated.

This second report describes in detail the treatment of the experimental data on *P-V-T* properties and the calculation of the related thermodynamic properties, and to give the results for methane and ethane. The work on the other compounds in the program, propane, *n*-butane, isobutane, *n*-pentane, etc., is similarly planned and will be reported in later papers.

PROPERTIES TABULATED

The properties for which values for *P-V-T* and related properties are given in the tables of the API Research Project 44 are listed in detail in Table I, including the name, symbol, and units for the property, the units of temperature and pressure, and the letter identifying the given table.

The definitions of the thermodynamic symbols and standard states are given by Lewis and Randall (*13*), and Rossini (*18*), and in the earlier report (*7*).

In connection with the standard state for tables in which pressure is given in pounds per square inch, it should be noted that the standard state is the hypothetical state where the fugacity is 1 in the given units, in this case where the fugacity is 1 p.s.i.

METHOD OF CALCULATION AND EQUATIONS INVOLVED

In the present report, only the region of "superheated" vapor is treated, with the discussion of the liquid and two-phase region being reserved for a later time.

The several investigators generally use different forms and values of the variable in making the measurements and reporting the results. For proper comparison of such heterogeneous data, a convenient and powerful method is to use an appropriate equation of state as a reference frame and to calculate the difference between the observed values and the corresponding ones given by the reference frame.

The equation of state used as the reference frame need not be one which reproduces the data accurately. Indeed, this might be an impossible requirement, since no known equation of state reproduces the most accurate data within the limits of uncertainty. The most useful property to use in evaluating that difference between the observed experimental value and the value calculated from the reference equation of state is that of volume, either molal or specific.

For the present work, the Benedict-Webb-Rubin (BWR) equation of state was selected to provide the reference frame because it reproduces the general character of *P-V-T* relationships better over a wider range of temperature and pressure than any of the other equations of state of similar complexity:

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + (cd^3/T^2)(1 + \gamma d^2)e - \gamma d^2 \quad (1)$$

In Equation 1, R, P, T, and d are the gas constant, pressure, temperature, and density, respectively, and a, b, c, A_o, B_o, C_o, α, and γ are constants.

For the present work, it is necessary only that the selected set of constants to be used for the BWR equa-