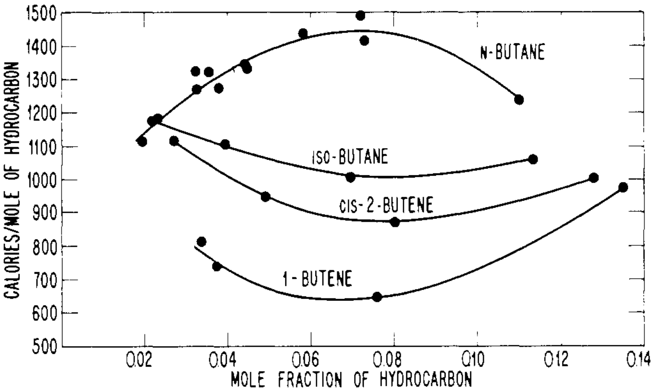

Figure 3. Intregal heats of mixing of C_4 hydrocarbons in water-acetone solvent

addition of *n*-butane to it in some manner which differs from the change found when the other three C_4 hydrocarbons are added.

In conjunction with comparisons between the energies of mixing established directly through calorimetry and from vapor liquid equilibria, other systems were investigated. The molar integral heat of mixing of *n*-butane in furfural was found to be 1298 calories per mole at the 0.010 mole fraction level of hydrocarbon. From vapor-liquid equilibria Mertes and Colburn (*1*) concluded the value to be 1668 calories per mole. Likewise, the calorimetric and calculated values for the heat of mixing of 2-methylpropane are 1234 and 1659 calories per mole, respectively; for 1-butene the quantities are 1199 and 1094 calories per mole.

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Supersaturation in Hydrocarbon Systems

n-Pentane–Silica

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NICHOLS RECENTLY reviewed the experimental work associated with the supersaturation of hydrocarbon liquids (*9*). Silvey and coworkers studied supersaturation in the methane-*n*-decane system (*14*). Kennedy and Olson (*5*) established that it was possible to maintain hydrocarbon liquids at pressures markedly below bubble point for short periods of time. Marboe and Weyl (*8*) made some investigations of the influence of solid surfaces upon the duration of a specified degree of supersaturation in liquids.

The molecular theory of liquids (*3, 6, 7*) is based upon the concept that significant local fluctuations in the state variables are to be expected at a point as a function of time. Such fluctuations result in marked differences in the time during which a thermodynamic system may be maintained in a strained condition at an invariant macroscopic state. This time of strain is random in time (*4, 9*) and follows Poisson's distribution (*9*). A reconnaissance study has been made of the *n*-pentane-silica system at 160° F. Regression analysis of the experimental information substantiates in part that the time of strain is random with respect to time. No review of the statistics (*4, 9*) will be given here. The methods of regression analysis set forth by Nichols (*9*) will be employed in the analysis of the results.

METHODS AND EQUIPMENT

In principle, the method involved placing a quantity of *n*-pentane and silica in a spherical, isochoric vessel and adjusting the temperature so that the system was maintained under a desired strain. The time required for the formation of the first bubble was noted. Measurements using this equipment were first made with *n*-pentane alone and later with a mixture of *n*-pentane and a substantial quantity of finely divided silica. The primary objective was to establish the order of magnitude of the effect of silica upon the time of strain for a particular degree of supersaturation.

Figure 1 portrays the details of the arrangement of the isochoric pressure vessel. It is constructed of 347 stainless steel and was provided with a slack diaphragm which permitted the pressure in the system to be measured with a pressure balance (*13*). In the case of most of the results reported here for the *n*-pentane-silica system, the isochoric vessel was connected also by means of a stainless steel tube 0.070 inch in diameter to a mercury U-tube to permit the pressure variations within the system to be measured as a function of time. The other arm of the mercury U-tube was connected to a manostat which has been described (*10*). This manostat, which involved a slack diaphragm and an isochoric vessel filled with nitrogen, made it possible to determine readily variations in pressure of the order of 0.01 p.s.i. The variations in pressure with time of the strained system were recorded upon a conventional strip-recorder.

The temperature of the system was known within 0.01° F. in relation to the international platinum scale (*1*). Pressures were measured within 0.1 p.s.i. relative to the vapor pressure of carbon dioxide at the ice point (*2*).

The net volume of the isochoric vessel, with no silica present, at a temperature of 160° F. and a pressure corresponding to the vapor pressure of *n*-pentane was 0.008541 cubic foot. The details of the equipment have been published (*13*). The interior surface of the vessel was 0.25 square foot. This included the area of two steel balls approximately 0.75 inch in diameter which were used to agitate the *n*-pentane and the *n*-pentane-silica systems

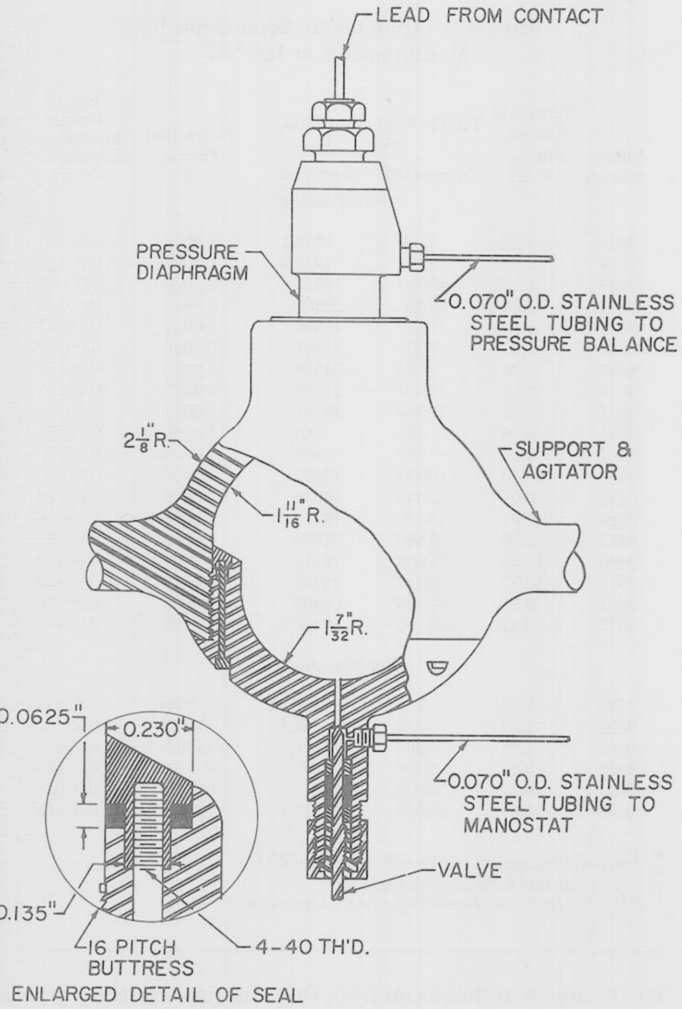

Figure 1. Details of isochoric pressure vessel

by oscillating the vessel as desired. The samples were conditioned at a pressure of 1000 p.s.i. above the bubble point of *n*-pentane for 2 hours after the attainment of thermodynamic equilibrium, with intermittent agitation, before determining the time of strain for a given supersaturation pressure. This period of conditioning was sufficient to bring the *n*-pentane–silica system to equilibrium either upon increase or decrease of pressure. Measureable changes in pressure with time were encountered for periods of several hours after the attainment of thermal equilibrium. In the isochoric vessel there were 29.4 square feet of metal surface per cubic foot of contents.

MATERIALS

The *n*-pentane, pure grade from the Phillips Petroleum Co., was reported to contain less than 0.01 mole fraction of material other than *n*-pentane. It was deaerated and introduced into the isochoric vessel by conventional weighing bomb techniques (*12*). The deaerated sample showed a specific weight at atmospheric pressure and 77° F. of 38.775 pounds per cubic foot, as compared to a value of 38.791 pounds per cubic foot reported by Rossini (*11*) for *n*-pentane at the same temperature. An index of refraction relative to the *D*-lines of sodium at 77° F. of 1.3547 was obtained from the sample as compared to a value of 1.35472 reported by Rossini for an air-saturated sample. The vapor pressure of this sample at 160° F. was 42.5 p.s.i., which agrees satisfactorily with accepted values.

The silica (New Jersey Silica Sand Co.) had a specific surface of 3515 square feet per pound as determined by krypton adsorption techniques. Photomicrographs of the silica, magnified 20 and 200 times, are shown in Figure 2. The silica was repeatedly leached with hydrochloric acid and, after washing with distilled water, was dried and heated to a temperature of 500° F. for approximately 30 hours at a pressure which reached a minimum value below 10^{-6} inch of mercury. The silica was stored in sealed glass containers until ready for use. Microscopic examination of the silica before and after use in the isochoric equipment indicated no significant change in the specific surface as the result of any grinding action between the steel agitators and the walls of the vessel.

PROCEDURE

The isochoric vessel was first filled with pure *n*-pentane and the supersaturation characteristics of this sample were determined at a temperature closely approximating 160° F. The sample was first heated to such a temperature that the pressure was approximately 1000 p.s.i. The temperature of the sample was then gradually decreased until the pressure within the isochoric vessel reached as value yielding the desired strain. Isothermal conditions were then maintained, and the time required for the formation of the first bubble was determined.

After the supersaturation characteristics of this sample of *n*-pentane in the isochoric vessel had been compared with earlier measurements (*9*), the *n*-pentane was removed and the isochoric vessel nearly filled with silica. A total of 0.5461 pound of silica was introduced. The entire system

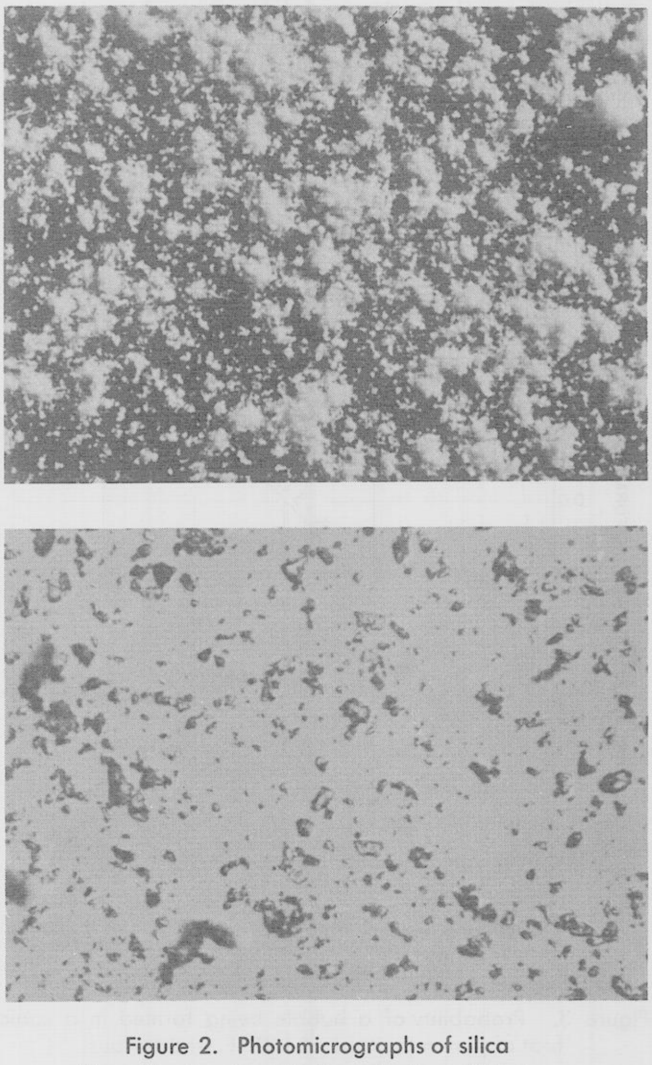

Figure 2. Photomicrographs of silica
Magnification: top, 20 times, bottom, 200 times

was then heated to a temperature of 220° F. and evacuated to a pressure below 10^{-6} inch of mercury for 24 hours. The *n*-pentane was then introduced by conventional high-vacuum techniques and the supersaturation measurements repeated. As indicated earlier, the sample was conditioned at a pressure of 1000 p.s.i. for a period of 2 hours with intermittent agitation before the temperature was reduced. Earlier work (*9*, *14*) indicated that longer conditioning periods at elevated pressures did not materially influence the statistical distribution of time of strain. In all cases, the reported value of the supersaturation pressure was based upon the vapor pressure of pure *n*-pentane at the temperature in question.

EXPERIMENTAL RESULTS

The experimental results associated with measurements of the supersaturation of pure *n*-pentane in the isochoric system at 160° F. are recorded in Table I. In all statistical treatment, the data of Table I were combined with earlier measurements (*9*) upon *n*-pentane at 160° F. This procedure yielded a better confidence limit in the statistical evaluation of the behavior than if the present data were used independently. Data for *n*-pentane in a spherical steel vessel obtained in an earlier study (*9*) were used in predicting the behavior of *n*-pentane at a supersaturation pressure of 5 p.s.i. Insofar as could be ascertained, the agreement between the earlier and the present measurements was within the confidence limit expected for the combined set of data. All of the data were reduced to correspond to a supersaturation pressure of 5.0 p.s.i. by application of the Arrhenius relation (*9*) to each set of data. The applicability of the Arrhenius relation in such a situation is open to much uncertainty but has been employed until additional data are available to support a more accurate description of the behavior. The constant for the Arrhenius relation was established fron earlier measurements (*9*).

The conversion to the basis of 1 cubic foot of *n*-pentane was made upon the assumption that the time for the formation of a bubble under a given condition of strain is inversely proportional to the total volume of the system. Such an approach appears reasonable when the nature of the phenomena is considered. The formation of bubbles is assumed to be random in time and in space, which accounts for a linear relationship between the reciprocal of the mean time for the formation of a bubble and the total volume of the system.

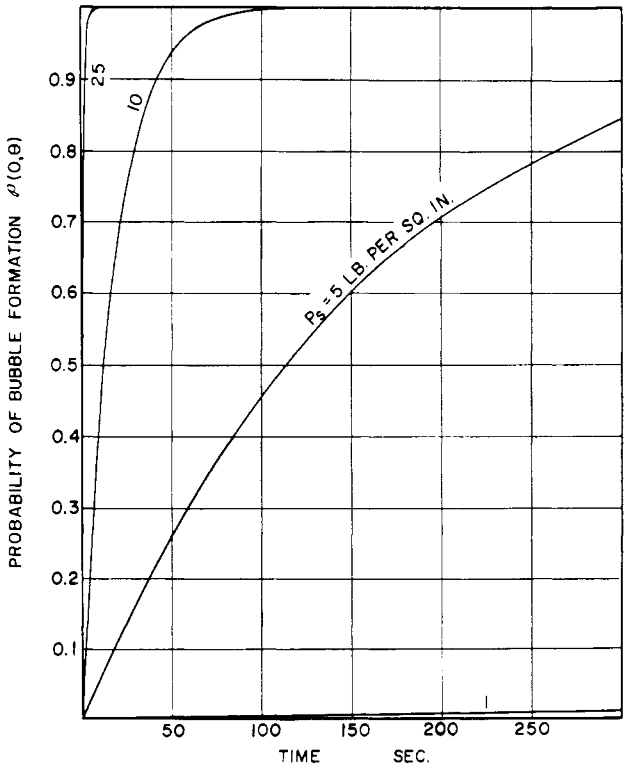

Figure 3. Probability of a bubble being formed in a cubic foot of pure *n*-pentane at 160° F. and various supersaturation pressures

Table I. Experimental Supersaturation Measurements at 160° F.[a]

Identification	Supersaturation Pressure, P.S.I.	Bubble Formation Time, Sec. Uncorrected	Bubble Formation Time, Sec. Corrected	Correction Factor, β	Rate of Bubble Formation, Bubbles/Sec. Cu. Ft.
		Pure *n*-Pentane[a]			
9303	5.24	1200	1202.2	1.0018	0.09739
9313	5.64	2220	2225.9	1.0027	0.05260
9329	4.50	17040	16982	0.9966	0.00689
9325	4.83	22620	22582	0.9983	0.00520
9345	5.19	46200	46300	1.0022	0.00253
9341	4.48	48600	48431	0.9965	0.00242
9358	4.90	74580[b]	74525	0.9993	0.00157
9366	4.88	75600[b]	75500	0.9987	0.00155
9337	5.58	79200[b]	79291	1.0011	0.00148
9401	9.86	360	360	1.0000	0.32523
9397	9.96	660	660	1.0000	0.17740
9385	10.46	10800	10807	1.0006	0.01083
9405	10.01	12000	12000	1.0000	0.00976
9389	9.91	18420	18420	1.0000	0.00636
9417	9.96	37680	37680	1.0000	0.00311
9409	10.33	72000[b]	72010	1.0001	0.00163
9413	10.57	73620[b]	73709	1.0012	0.00159
9381	9.74	80400[b]	80400	1.0000	0.00146
9377	10.41	82800[b]	82857	1.0007	0.00141
		n-Pentane–Silica[a,c]			
9486	1.17	120	130.31	1.0859	1.47379
9490	1.04	240	244.68	1.0195	0.78490
9462	1.12	960	1022.4	1.0650	0.18784
9470	0.81	2700	2298.3	0.8512	0.08356
9494	0.89	12900	11907	0.9230	0.01613
9498	1.07	24060	25082	1.0425	0.00766

[a] Isochoric equipment with a volume of 0.008541 cu. ft.
[b] No bubble had formed up to this time.
[c] 0.003333 cu. ft. of silica with a surface area of 1919.6 sq. ft.

Figure 3 depicts the probability of a bubble being formed per cubic foot of pure *n*-pentane. These values were calculated from the data of Table I and earlier measurements (*9*). Supersaturation pressures of 1, 5, 10, and 25 p.s.i. have been included.

The experimental results obtained with the mixture of *n*-pentane and silica are set forth in Table I. An effort has been made to present these results in much the same form as the *n*-pentane alone. In this instance it was not possible to carry out significant measurements at tensions much in excess of 1 p.s.i. However, upon the assunption that the Arrhenius equation applies to the effect of supersaturation pressure upon time strain, it is possible to reduce the data at conditions of strain varying between 0.81 and 1.17 p.s.i. to correspond to a nominal value of 1 p.s.i. The constants of the Arrhenius equation were taken from the earlier study of *n*-pentane (*9*). The corrected values of time of strain are included in Table I.

The probability of a bubble being formed in a cubic foot of *n*-pentane when in contact with 370,000 square feet of silica, for a supersaturation pressure of 1 p.s.i., is shown in Figure 4. The corresponding behavior for *n*-pentane when not in contact with silica, for supersaturation pressures of 1 and 5 p.s.i., is also shown.

The mean time for formation of a bubble for 1 cubic foot of pure *n*-pentane at a supersaturation pressure of 1 p.s.i.

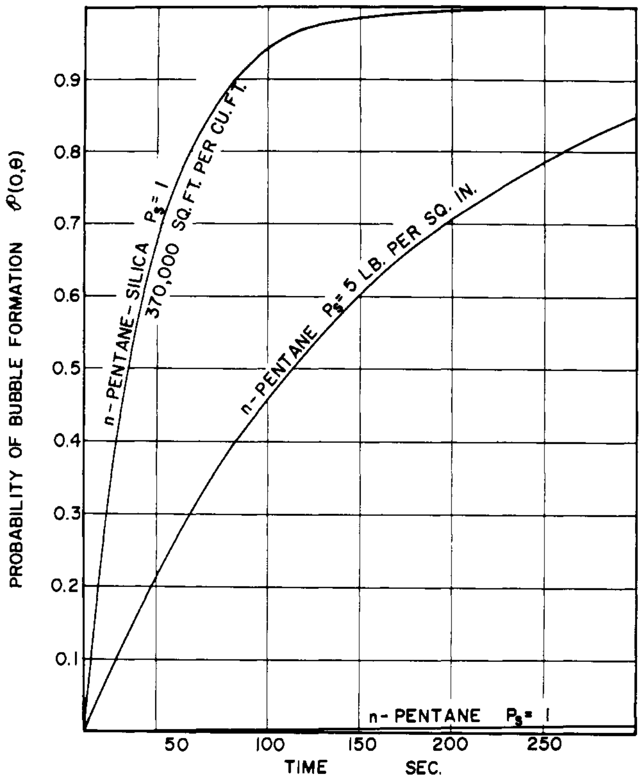

Figure 4. Probability of a bubble being formed in a cubic foot of *n*-pentane at 160° F.

would be 2.74×10^4 seconds, corresponding to 7 hours and 37 minutes, which may be compared to a mean time of 35 seconds associated with 1 cubic foot of *n*-pentane in contact with 370,000 square feet of silica. As a first approximation, the above area of silica per cubic foot of *n*-pentane decreases the attainable supersaturation pressure for a probability of bubble formation of 0.5 by a factor of 9. Such a marked change is significant and indicates that surface area may influence markedly the time of strain attainable with hydrocarbons. Such results are indicated by the work of Marboe and Weyl (*8*). The conditions associated with their investigation were sufficiently different, however, from those encountered in this study as to render direct comparison unprofitable. Earlier work (*9, 14*) did not permit the effect of a fivefold change in the area of the steel vessel exposed to hydrocarbon per unit volume of liquid phase to be detected. In the present study, the relatively large interfacial area between the silica and hydrocarbon apparently introduced a significant effect.

NOMENCLATURE

P = pressure, p.s.i.
P_s = supersaturation pressure, p.s.i.
$p()$ = probability of a bubble being formed
β = correction factor
θ = time, sec.

ACKNOWLEDGMENT

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CORRECTION

In "Solubility of 1, 3-Butadiene in Water" [C. D. Reed and J. J. McKetta, J. Chem. Eng. Data **4**, 295 (1959)], Figure 3 is incorrect and should appear as follows.