CONCLUSIONS

The experimental data, when extrapolated to zero feed volume and plotted on a vaporization-composition diagram like Figure 5, indicate the validity of the following generalizations:

1. The change of residual spray composition with vaporization is a function of initial composition, chamber air temperature, and nozzle characteristics for the particular binary, in this case ortho-dichlorobenzene-tetrachloroethylene.
2. The other variables investigated—feed pressure, feed temperature, and nozzle-to-tray distance—have the effect of locating the position on the vaporization-composition curve but do not affect the shape of the curve.

The calculated results for the binary based on the assumption of liquid-diffusion-controlling mass transfer indicate the smaller droplets slowing down, increasing in temperature, changing in composition, and decreasing in radius more rapidly than the larger drops. Such behavior is consistent with experience. Comparison of the calculated data with experimental results as shown on a vaporization-composition diagram indicates agreement during the first five inches of nozzle-to-tray height. It appears that a thermal conduction and liquid diffusion mechanism may control the drop vaporization, at least for these first five inches.

Further experimental work seems to be justified to determine more precise values of drop-size distribution, initial drop velocities, and liquid diffusion coefficients. Recalculation with the more correct values could possibly result in better agreement between the calculated and experimental values and give additional support to the proposed vaporization mechanism.

ACKNOWLEDGMENT

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NOTATION

A = area
C_p = heat capacity at constant pressure
d = drop diameter
D = diffusion coefficient
f = friction factor
g = gravitational constant
h = heat transfer coefficient
k = thermal conductivity
L = length
m = mass
M = molecular weight
r = drop radius
t = temperature
Δt = temperature difference, air-to-drop surface
u = velocity
x = mole-fraction high boiler
α_L = liquid thermal diffusivity
θ = time
λ = latent heat of vaporization
ρ = density

Subscripts

a = air
b = boiling point
h = horizontal
L = liquid
m = mean
0 = initial
v = vertical
HB = high boiler
LB = low boiler

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Evolution of Gas from Liquids Flowing through Porous Media

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The production of oil and gas by pressure depletion involves both the formation of bubbles and the diffusion of gas from the liquid phase into these bubbles. Studies were undertaken to outline in detail the process of bubble formation when the driving force is small. This work shows that the formation of bubbles is a random process which can, however, be described by a simple probability distribution function. Also, calculations have been made to determine how fast gas will diffuse into uniformly distributed gas bubbles.

These results make it possible to describe the manner in which a gas phase is established during the pressure depletion process. In this process the rate of pressure decline is the most important factor influencing the total number of bubbles produced. Laboratory tests have substantiated the finding that in certain types of porous media the amount of oil recovered is sensitive to the number of bubbles formed.

Oil is produced from many petroleum reservoirs by a solution-gas-drive process. In this production mechanism the underground oil is pushed out and replaced by its own dissolved gas when pressure on the reservoir is reduced. A typical oil field for which this process is operative is characterized by constant reservoir volume and is usually discovered at a pressure above the bubble-point pressure of the crude oil. When well-bore pressure is reduced, oil at first is produced by virtue of its expansibility. However, as pressure declines below the bubble-point pressure the same rate of oil production can be realized with a smaller amount of pressure decline provided that gas evolves within the reservoir and replaces the oil withdrawn. The purpose of this paper is to consider the factors which are important in the formation of such a gas phase and to describe quantitatively the mechanism by which this gas is evolved.

The establishment of a gas phase depends first upon the formation of small bubbles of gas. These bubbles subsequently expand to drive out oil. Expansion of the gas bubbles results from both reduction in pressure and inward diffusion of gas from the locally supersaturated oil. The development of a gas phase in this manner is therefore a rate process and must be clearly understood in order that laboratory solution-gas-drive tests may be made to yield results which will be representative of oil-field performance. Furthermore, it is commonly assumed that gas and oil are always in equilibrium within a reservoir at the average hydrostatic pressure. If appreciable nonequilibrium does occur, then reservoir performance predictions cannot be accurately made unless these deviations are resolved.

Little information is presently available concerning bubble formation and diffusion as they occur in petroleum reservoirs (*1, 4, 5, 6, 11*); however, it is known that both bubble-formation rates and diffusion rates depend strongly upon the degree of supersaturation. Both tend to counteract a reduction in hydrostatic pressure below the bubble-point pressure. Diffusion acts in a direct manner and bubble formation acts by reducing the length of the diffusion paths. Thus the following simplified concept of the solution-gas-drive process is probably qualitatively correct. This is the concept upon which this paper is developed.

The withdrawal of oil from a reservoir results in a decrease in the reservoir pressure. Soon reservoir pressure falls below the bubble-point pressure of the oil. The oil then is supersaturated, and bubbles begin to form at a rate depending upon the magnitude of this supersaturation. As soon as the first bubbles are evolved, a free gas phase exists and dissolved gas begins to diffuse out of the oversaturated oil into the gas bubbles. This process tends to return the system to equilibrium, albeit slowly, as only a few bubbles are present at this early stage and diffusion paths are therefore quite long. In other words, in the early stages of depletion the bubble-point pressure of the oil cannot be lowered by diffusion so fast as the static reservoir pressure is falling because of withdrawal of fluid. During this time the average supersaturation in the reservoir therefore rises, and additional bubbles form at an ever-increasing rate owing to this increase in supersaturation. The result is a rapid increase in the number of bubbles present. As this occurs, the average distance the gas must travel in diffusing out of the oil and into the bubbles diminishes. There is, therefore, a rapid increase in the quantity of gas transferred by diffusion and, consequently, an increase in the rate at which the average reservoir bubble-point pressure is reduced. Eventually diffusion assumes sufficient importance so that the bubble-point pressure of the oil, falls more rapidly than does the reservoir pressure, and the average supersaturation begins to decline. As soon as supersaturation declines sufficiently, bubble formation ceases for all practical purposes. After this, and throughout the remainder of the life of the reservoir, the rate of diffusion is adequate to reduce the bubble-point pressure of the oil at least as fast as the reservoir pressure is decreased.

Practically speaking, it is impossible in the laboratory to scale the processes described above. In order to study experimentally the formation of a gas phase in a reservoir, therefore, it is necessary to use reservoir rates of pressure decline. As these are impractical for laboratory work, it accordingly becomes highly desirable to develop an analytical technique for estimating the behavior of a system under such conditions.

A quantitative analytical description of this process has been given by Kennedy and Olson (*6*). However, their experimentally determined relation between supersaturation and rate of bubble formation leads to what appears to be an erroneous conclusion. These authors conclude that supersaturation in excess of 31 lb./sq. in. cannot exist, even for a few days, at any point in a reservoir. This observation is based upon the following data given in their paper: (1) at supersaturations of less than 31 lb./sq. in., the rate of bubble formation is zero; (2) as the supersaturation is increased to about 31 lb./sq. in., the rate of bubble formation suddenly becomes very large; (3) at supersaturations in excess of 31 lb./sq. in., bubble-formation rates increase with extreme rapidity. In other words, these authors assume that virtually all bubbles are formed instantaneously when the amount of supersaturation reaches 31 lb./sq. in. As a first approximation this assumption is valid, at least in the range of rates of pressure decline encountered in the field. However, it is no longer valid when laboratory rates of depletion are considered for which experimentally observed supersaturations in excess of 100 lb./sq. in. are common (*8*). An improvement on Kennedy and Olson's treatment of pressure-depletion nonequilibrium behavior is, therefore, needed in order to have confidence in comparisons between laboratory and field behavior. This is particularly important as it has been shown (*9*) that in some laboratory tests the total oil recovery by depletion depends strongly upon the number of gas bubbles formed within the oil-bearing medium. Until such laboratory phenomena are adequately understood and controlled, considerable uncertainties will remain in the prediction of depletion-drive-oil-recovery performance for certain types of reservoirs.

A study of the literature reveals that little information has been developed concerning the mechanism of bubble formation. Although some experimental data are available (*6, 11*), these data are not complete enough to include rates of bubble formation as slow as those normally encountered in petroleum reservoirs. Such data are exceedingly difficult to obtain. Furthermore, the available data show a certain lack of reproducibility which is difficult to dispose of by assuming that experimental errors are responsible. Accordingly, a large fraction of the effort reported in this paper was devoted to a study of the fundamental aspects of bubble formation in quiescent oil-gas solutions. The theoretical relations which were developed have been confirmed by experiment, and as a result it is now possible to assess the reliability of data given in the literature concerning the effect of supersaturation on the average rate of formation of gas bubbles.

Some additional data have also been obtained for bubble-formation rates vs. supersaturation. Comparison with published data (*11*) shows that bubble formation in most reservoirs can probably be predicted adequately on the basis of the information presently available. However, in order to predict the manner and rate at which a gas phase forms on pressure reduction, an improved method of calculating the interaction of diffusion and bubble formation was developed. This calculation permits complete prediction of the nonequilibrium behavior of a gas-oil solution undergoing pressure reduction.

This discussion which follows has been divided into four sections in the interest of clarity. These deal, respectively, with (1) the statistical nature of bubble formation, (2) the effect of supersaturation on the average rate of formation of bubbles, (3) the effect of diffusion on the growth of the bubbles and upon local supersaturation, and (4) prediction of the nonequilibrium behavior of a gas-oil mixture during pressure decline, insofar as bubble formation and diffusion are important.

STATISTICS OF BUBBLE FORMATION

Theoretical

To predict the nonequilibrium behavior expected during a pressure-depletion drive, information is needed concerning the rate of bubble formation as a function of supersaturation. Any experimental study of bubble formation involves the determination of the rate of bubble formation under a fixed set of conditions*.

Attempts to define precisely this relationship in the laboratory by measuring the time required to form single bubbles are generally not fruitful. That is, if several identical experiments are made, the reciprocal of the average time required for the first bubble to form should be representative of the rate of bubble formation under the conditions being studied. How good this value is, however, is questionable when it is found that these nucleation times vary over an extremely wide range for statistically identical experiments. For example, it is not unusual in a set of three carefully controlled experiments to obtain single-bubble-formation times which differ by a factor of ten. Because of this apparent lack of reproducibility, little confidence can be placed in such measurements without a basic knowledge of the mechanism of bubble formation. Fortunately this question can now be resolved on the basis of a mathematical study of the statistics involved. The results of this study, as described below, give a means of interpreting the observed variations and of placing confidence limits on the measured average values of bubble-formation rates.

The formation of a bubble in the absence of external sources of energy† occurs only upon the appearance of a critical local fluctuation in energy and density. According to the kinetic theory of matter, local fluctuations in energy and density are completely random. This implies that the probability of a critical fluctuation occurring during a unit of time, Δt_i, under a given set of fixed conditions is a constant, p', which depends only on length of the time interval. Thus the probability of *no* bubble forming in the first unit of time, Δt_1, is q (where $q = 1 - p'$). In the second unit of time, Δt_2, it is also q. The probability that bubble formation has not occurred *by the end of the second unit of time* is $q \times q = q^2$. In a similar manner, the probability that no bubbles have formed *by the end of t units of time* is q^t and by the end of $t + \Delta t$ units of time is $q^{t+\Delta t}$. The probability that a bubble was first formed during the time interval of t to $t + \Delta t$ is therefore the difference of these two terms.

$$P(t, t + \Delta t) = q^t - q^{t+\Delta t} \qquad (1)$$

The probability density associated with this probability is therefore

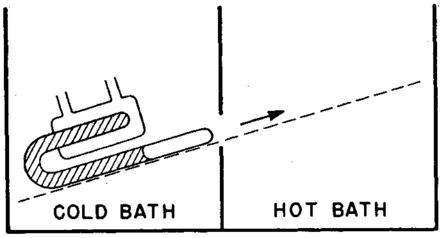

Fig. 1*a*. Position of *J* tube with heating jacket prior to bubble-formation experiment.

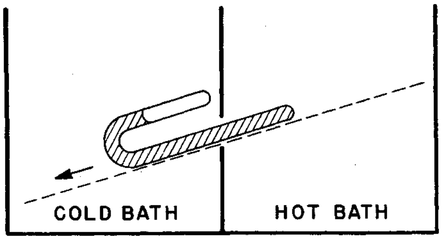

Fig. 1*b*. Position of *J* tube during bubble-formation experiment.

$$\Phi(t) = \lim_{\Delta t \to 0} \frac{P(t, t + \Delta t)}{\Delta t}$$

$$= -\frac{d}{dt}(q^t) \qquad (2)$$

If $q = e^{-\alpha}$, this becomes

$$\Phi(t) = \alpha e^{-\alpha t} \qquad (3)$$

In this expression α is a parameter, the physical significance of which will be made clear in the subsequent discussion.

For many identical experiments, the *mean* time required for one bubble to form may be determined from the following relation:

$$\bar{t} = \int_0^\infty t\Phi(t)\, dt$$

$$= \int_0^\infty \alpha t e^{-\alpha t}\, dt = \frac{1}{\alpha} \qquad (4)$$

This result shows that the parameter α is equal to the reciprocal of the mean time required for one bubble to form. Alternately, for a large number of identical experiments, α may be identified with the mean or average rate at which bubbles appear. (Only the first appearance in each experiment is counted, for the reasons noted above.)

The *variance* associated with the measured time is

$$\sigma^2 = \int_0^\infty (t - \bar{t})^2 \Phi(t)\, dt$$

$$= \int_0^\infty (t - \bar{t})^2 \alpha e^{-\alpha t}\, dt = \frac{1}{\alpha^2} \qquad (5)$$

and the standard deviation σ of the measured times is

$$\sigma = \frac{1}{\alpha} \qquad (6)$$

This result shows that the *standard deviation is numerically equal to the mean time required for the first bubble to form.*

Equation (3) therefore predicts an inherent nonreproducibility which will be observed in studies of average bubble-formation rates. Another way of looking at this result is to consider the percentage of runs in which bubble formation will occur within specified intervals of time. The probability that the first bubble will form in less than one-half the mean time is 0.39 [obtained by integrating Equation (3) between the limits $t = 0$, and $t = \frac{1}{2}d$]. This means that in 39% of the runs the first bubble is expected to form in less than one-half the mean time. Similarly, it is found that 23% of the runs are expected to last longer than one and one-half times the mean. It is not surprising, therefore, that in a series of identical runs wide variations are found in the time required for one bubble to appear.

The validity of the foregoing probability distribution function can be properly tested only if data are obtained by an experimental method in which all variables can either be controlled or their effect ascertained. Once the validity of Equation (3) has been established, rate of bubble-formation data collected by other methods can then be properly analyzed and their accuracy determined. The following discussion presents experimental data which were collected solely to test the theoretical relationships established above.

Experimental

The experimental method used in the present investigation involved superheating liquid propane sealed inside glass tubes.

Pyrex-glass capillary tubing (2 by 8 mm. in diameter and 40 cm. long) cleaned in hot chromic acid cleaning solution and thoroughly rinsed in distilled water was sealed at one end and bent in the form of a *J*, the short leg being the sealed end. The tube was then sealed to a high-vacuum system. After thorough evacuation ($< 10^{-6}$ mm. Hg) at 500°C., propane (Phillips 99 mole %), which had been purified by repeated high-vacuum transfers, was condensed in the tube and the long arm sealed while the tube was still under high vacuum. The completed *J* tube after removal from the vacuum system was then ready for repeated studies.

A double water bath was constructed from a rectangular aquarium by adding a vertical partition consisting of a sheet of rubber sandwiched between two sheets of Bakelite and containing a horizontal row of six holes. The long arm of each of six *J* tubes was slid through a hole in the partition and its end securely fastened to a sliding rack mounted in one of the baths. Thus moving the rack simultaneously moved the long arms of all six *J* tubes in or out of one of the baths while the short arms always remained in the other bath. The baths were vigorously stirred, and temperatures were controlled to better than ±0.01°F. by means of mercury thermoregulators and a large heat sink.

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*In an actual experiment, as soon as the first bubble forms the conditions of the experiment change owing to diffusion and the results no longer clearly show the relation between supersaturation and bubble-formation rates. The only useful information obtainable from such an experiment is the time required for the first bubble to form.

†D. A. Glaser has found (*3*) that cosmic rays can initiate bubble formation in superheated liquids. These rays are a possible external energy source which, however, would not change the statistics of bubble formation, because, like fluctuations within the liquid, cosmic rays are random.

The J tubes, installed in the dual water bath, were prepared for a run by heating the short arms with hot water flowing through jackets slipped over them as shown schematically in Figure 1A. In this manner all vapor in the long arms was condensed, only vapor in the short arms being left. After removal of the heated jackets and establishment of thermal equilibrium, the long arms were drawn into the hot bath (*see* Figure 1B) and the time required for bubble formation observed.

The propane in the long arm became superheated on being drawn into the hot bath as the vapor-liquid interface remained in the cold bath. Of course, as soon as bubble formation occurred, all vapor in the cold bath was condensed and equilibrium established, ending the run. Since the density of the liquid propane in the hot bath was less than that in the cold bath, it was necessary to incline the J tubes as shown in order to avoid convection currents. For a similar reason, it was necessary to avoid the possibility of the vapor in the short arm moving into the hot bath. This was accomplished by using tubes bent in the form of a J.

A dummy J tube, containing a thermocouple and filled only with atmospheric air, was used to determine the temperature distribution across the partition of the dual bath. The temperature gradient was found to extend less than 1 cm. away from the partition. During a run the long arm of the J tube extended 8 cm. into the hot bath. However, since the temperature transition zone extended 1 cm. into the hot bath, the column of liquid propane which was superheated from the cold-bath temperature to that of the hot bath was 7 cm. long and the volume of liquid propane was 0.22 cc. Rate of bubble-formation data obtained by use of these J tubes can, therefore, be expressed as bubbles per second per cubic centimeter by dividing the results by 0.22, the volume of superheated liquid propane studied. Additional measurements established that the time lag required for the arm to reach the desired superheat was satisfactorily small.

A series of runs was made on six J tubes containing propane superheated from 96.5° to 103.1°F. (p = 194.8 lb./sq. in. abs., p_h = 178.8 lb./sq. in. abs.). Each experiment was continued until bubble formation occurred. The results of these measurements are given in Table 1. The statistical tool known as the *analysis of variance* was used to determine whether or not all runs were statistically identical. The results of the analysis showed that the conditions from one set of six runs to the next might be considered identical but that runs for all the tubes might not. Two of the tubes, I and II, were apparently less stable than the other four tubes. The analysis of variance omitting these two tubes showed that the remaining four tubes could be considered identical and therefore only data obtained with these four tubes, III, IV, V, and VI, were considered in testing the applicability of Equation (3).

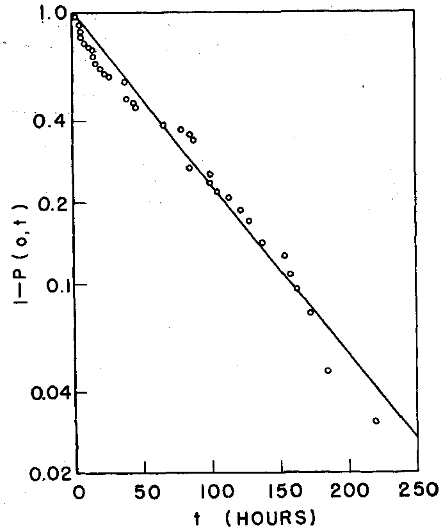

Fig. 2. Experimental bubble-formation data for liquid propane showing agreement with theory.

Equation (3) predicts the numerical equivalence of the mean time and the standard deviation. Experimentally the mean time (arithmetic average time) was 64.4 hr. and the calculated standard deviation in the observed time was 63.9 hr. Thus the requirement of the probability distribution function that the standard deviation be equal to the mean is met by the experimental data.

Integration of Equation (3) followed by rearrangement gives

$$1 - P(0, t) = e^{-\alpha t} \qquad (7)$$

where P (0, t) is the probability of bubble formation occurring in the time interval 0 to t. Thus a plot of log [1 − $P(0, t)$] vs. t should give a straight line with a slope of $-\alpha/2.303$. Such a plot of the data is shown in Figure 2. The solid line was obtained by least squares analysis of the data. Statistical t-tests applied to these data show that (1) there is no reason to assume that the intercept in Figure 2 is not unity or (2) that the slope is not $-\alpha/2.303$. In view of the agreement of experiment with theory, the probability distribution function developed in the previous section is considered to represent satisfactorily the behavior expected when experiments are performed to determine the time required for single bubbles to form. These results may therefore be used with confidence in planning and interpreting single-bubble experiments the objective of which is to relate average rate of bubble formation to the amount of supersaturation.

RATE OF BUBBLE FORMATION

A survey of the literature has revealed only a small amount of data relating rate of bubble formation to degree of supersaturation. Much is available concerning so-called "limiting" supersaturation attainable, but these data are not of interest in the present problem. Of pertinent interest are the data of Kennedy and Olson (*6*) on methane-kerosene solutions and of Wood (*11*) on a crude oil from the Rangely Field, Colorado. Both sets of data show considerable scatter in the experimentally reported bubble-formation times, but this apparent uncertainty is not inconsistent with the theory developed above. The data of Wood are of particular interest as they represent the only presently available information relative to formation of bubbles in a crude oil-gas solution contained within a porous rock. It would be highly desirable to be able to use these data in predicting the performance of perhaps many different oil reservoirs, but this can be done only if rates of bubble formation do not differ widely from one crude oil to the next.

In order to determine reasonable limits of variation of nucleation rates for crude oil-gas solutions, bubble-formation data

TABLE 1. HOURS REQUIRED FOR FIRST BUBBLE FORMATION IN LIQUID PROPANE SUPERHEATED FROM 96.5° TO 103.1°F.

(Data in each row were obtained from experiments begun simultaneously on each of the six presumably identical tubes. A range of values indicates that bubble formation occurred within the given range.)

Tube					
I	II	III	IV	V	VI
1.6	24.4	23	22.8	47	128–175
5.8	30.5	4.8	4.0	56–71	32–48
5.7	4.5	1.8	8.0	32–95	8.2
0.8	2.0	1.3	32–48	5.3	100
7.8	8–24	4.2	32–48	8–24	8–24
1.0	26.9	179–192	104	104–121	32–96
2.5	8–71	6.0	100	80–96	5.7
0.3	1.8	56–120	32–48	56–120	152–168
4.8	32–46	56–118	124–132	176–192	224–287
0.5	3.0	51–117	3–18	149–163	19.8
8–23	32–48	121	56–120	32–48	8–23
3.5	5.0	6.5–22.5	29–46	219	6.5–22.5
0.4	1.3	128–144	172	201–264	27
1.0	56–72	6–22	1.0	56–72	1.0
1.2	5.0	7.0	79	5.0	80–94
0.8	1.0	4.0	8–24	136	45

were obtained for several typical solutions covering a moderate range of stock tank-oil properties. These data were obtained by rapidly lowering, to a predetermined value, the pressure on the fluid. Each solution was contained in a glass capillary formed into an inverted U tube. The time required for the first bubble to form in each test is given in Table 2. Calculated mean rates of bubble formation are presented in Figure 3, along with the data of Kennedy and Olson and of Wood. The vertical lines in Figure 3 encompass the 95% confidence limits. These were calculated by the relationship. $(1 - 2/\sqrt{n}) \leq J_t/J_0 \leq (1 + 2/\sqrt{n})$, which was obtainable in a straightforward manner by use of the method given in paragraph 6.12 of Wilks (*10*).

Some of the runs used to calculate the points shown in Figure 3 were not allowed to continue until bubble formation occurred. Even so, it is possible to use this incomplete information to obtain bubble-formation rates. All that is needed experimentally is the fraction of identical runs in which bubble formation occurs by the end of some fixed time t_x. Integration of Equation (3) between the limits 0 and t_x gives the relationship between this fraction and the rate of bubble formation:

$$\frac{x}{n} = P(0,\, t_x) = \int_0^{t_x} \alpha e^{-\alpha t}\, dt$$
$$= 1 - e^{-\alpha t_x}$$

where x/n is the fraction of runs in which bubble formation occurs by the end of time t_x. In addition to reducing the time required to make a number of runs, this method eliminates the necessity of continual observation during a run, as only its status (bubble formation or no bubble formation) at the end of time t_x need be known.

The relationship given above for confidence limits does not apply to the incomplete data just described. However, the binomial distribution function governs the statistical results of this latter type of test, as for each trial there are only two possible outcomes, success or failure of bubble formation by time t_x, and the probability of success does not change from trial to trial. According to Wilks (*10*), the 95% confidence limits for the binomial distribution are

$$\frac{\log\left(1 - \dfrac{x+2-2\sqrt{x+1-x^2/n}}{n+4}\right)}{\log\,(1 - x/n)} \leq \frac{J_t}{J_0}$$
$$\leq \frac{\log\left(1 - \dfrac{x+2+2\sqrt{x+1-x^2/n}}{n+4}\right)}{\log\,(1 - x/n)}$$

where x successes are observed in n trials lasting t_x days. Since $P(0,\, t_x) = x/n$, $J_0 = -(1/t_x) \ln\,(1 - x/n)$, according to Equation (7).

The Rangely system, as shown in Figure 3, appears to be less stable than the other crude systems. However, this can be explained on the basis of the large surface-to-volume ratio present when the former data were collected. These data were obtained by use of reservoir rock as the container, while a glass tube was used as a container for all the other data of Figure 3. It is known that solid surfaces decrease the stability of supersaturated solutions, but there is presently no definite information, either theoretical or experimental, as to the magnitude of the decrease.

In general, with exception of the Rangely data, the remaining crude-oil data of Figure 3 are seen to define a reasonable range of bubble-formation rates at any given supersaturation. Anticipating later results, it may be said that rates of bubble formation as a function of supersaturation will probably be nearly the same for most naturally occurring crude-oil–gas solutions. The exceptions will probably be high-shrinkage oils with relatively low interfacial tensions under reservoir conditions.

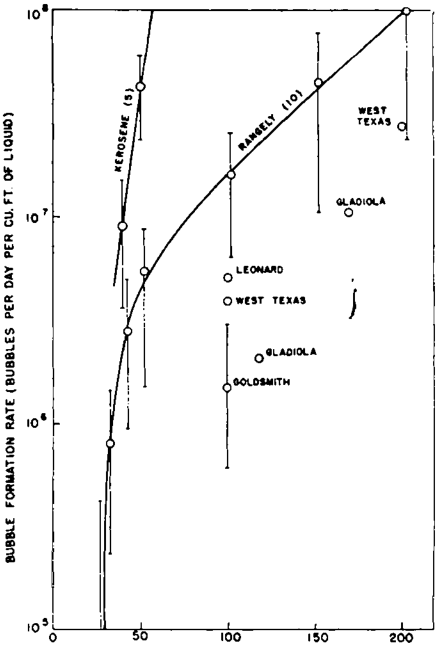

Fig. 3. Experimental bubble-formation data for several oil-gas solutions showing confidence limits on three systems. Confidence limits on the other systems are similar to those of Goldsmith.

TABLE 2. MINUTES REQUIRED FOR FIRST BUBBLE FORMATION IN A NUMBER OF CRUDE-OIL–GAS SOLUTIONS

(Volume of system = 1.6 cc.)

System number

1	2	3	4	5	6
1.0	<0.1	0.6	6.8	0.8	4.7
20.0	0.4	1.8	3.0	0.3	3.5
6.0	0.5	9.2	2.3	0.8	>20.0
9.5	0.2	0.3	2.3	1.5	19.8
4.3	0.5	5.0	14.0	3.8	12.0
6.0	<0.1	1.0	3.3	2.0	>20.0
2.3	0.4	17.5	4.3	0.3	3.0
1.7	0.2	8.2	4.0	5.8	0.3
11.0	6.8	1.8	68.0	8.8	>20.0
4.3	0.1	4.3	13.5	0.8	18.0

System 1—Methane and pipe-line oil (32°A.P.I.) from West Texas; room temperature; $p = 215$ lb./sq. in. abs., $p_h = 115$ lb./sq. in. abs.
System 2—Same as system 1, except $p_h = 15$ lb./sq. in. abs.
System 3—Methane and stock tank oil (37°A.P.I.) from Leonard Field, Okla.; room temperature; $p = 215$ lb./sq. in. abs., $p_h = 15$ lb./sq. in. abs.
System 4—Bottom-hole sample from Gladiola Field, N. M. (stock tank oil gravity = 48°A.P.I.); studied at bottom-hole temperature (177°F.); $p = 404$ lb./sq. in. abs., $p_h = 285$ lb./sq. in. abs.
System 5—Same as system 4, except $p_h = 235$ lb./sq. in. abs.
System 6—Methane and stock tank oil (32°A.P.I.) from Goldsmith Field, Texas; room temperature; $p = 215$ lb./sq. in. abs., $p_h = 115$ lb./sq. in. abs.

If the greater instability of the Rangely data is accepted as a manifestation of the large rock-surface area present during the experiments, then these latter data can be considered appropriate for use in predicting the nonequilibrium behavior to be expected in a majority of petroleum reservoirs. This is a particularly desirable approximation in view of the considerable expenditure of time and effort which is required for the collection of such data on any one system.

In spite of the good quality of the Rangely data, insufficient information is available at very small amounts of supersaturation, and this range is important for predicting reservoir performance. Nevertheless, nucleation theory predicts that nucleation rates will vary with supersaturation in the following manner:

$$\log J \propto (p - p_h)^{-2} \qquad (8)$$

when $(p - p_h) \ll p_h$. Within the limits of confidence of the Rangely data, this relationship is satisfied,* and it is has

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*This agreement of experimental data with nucleation theory is an indication that cosmic rays (*3*) were not an important factor in bubble formation in these experiments. There is the possibility, however, that cosmic rays were present in sufficient number to give an essentially continuous increase in energy available for bubble formation. This would result in smaller fluctuations causing bubble formation but would not change the variation of bubble-formation rates with supersaturation. Thus it is conceivable that bubble-formation rates within a petroleum reservoir are less than such rates observed in the laboratory under similar conditions.

been used to extrapolate Wood's experimentally determined rates to very small amounts of supersaturation. The uncertainty involved in making this extrapolation will be shown later to be only minor insofar as the nonequilibrium behavior of reservoir oils is concerned. For the purpose of calculations, the Rangely data will therefore be considered to be represented by the expression

$$\log J = 7.33 - 1.46 \times 10^3 (p - p_h)^{-2} \qquad (9)$$

DIFFUSION

When the pressure is changed in a system of coexisting gas and liquid phases, a state of nonequilibrium is created and diffusion occurs. The physical configuration of controlling interest in the initial development of a gas phase by pressure depletion is one of spherical symmetry, with gas diffusing from supersaturated oil into the bubbles. The rate of growth of the bubbles by inward diffusion of dissolved gas and the simultaneous depletion of the oil can be determined by appropriate solutions of the transient diffusion equation. It is here estimated that each bubble present may be isolated along with the oil surrounding it and that its behavior is typical of the total system.

Fick's hypothesis has been shown to hold for diffusion in porous media as long as an effective path length, or alternately an effective diffusion coefficient, is chosen (*1*, *7*). The following expression therefore will be considered a suitable description of diffusional transfer in porous media.* In this equation the

$$M_r = -D_e A \beta \frac{\partial p}{\partial r} \qquad (10)$$

reasonable approximation is made that $\partial c/\partial r = \beta(\partial p/\partial r)$ where p is the local bubble-point or saturation pressure. Combination of Equation (10) with a material balance over a differential element of volume leads to the following differential equation:

$$\frac{D_e}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial p}{\partial r}\right) = \frac{\partial p}{\partial t} \qquad (11)$$

In order to predict the amount of gas entering an isolated bubble and the resultant local decrease in the quantity of gas dissolved in the oil, Equation (11) must be solved subject to the following initial and boundary conditions. These are appropriate for the condition which exists when a bubble of radius a suddenly forms in the center of a gas-saturated sphere of liquid whose saturation pressure p_i is uniform. The outer boundary R of the liquid sphere is, because of symmetry, considered impervious to diffusion. The conditions of interest, therefore, are

$$p = p(r, t)$$

$$p(a, t) = p_h$$

$$\frac{\partial p}{\partial r}(R, t) = 0$$

$$p(r, 0) = p_i$$

The solution of Equation (11) subject to these conditions does not seem to be available in the literature but may readily be shown to have the following form:

$$\bar{p} = 1 - \frac{6}{(R/a)^2 + (R/a) + 1} \cdot \sum_{n=1}^{\infty} \frac{e^{-\gamma_n^2 D_e t/(R-a)^2}}{\gamma_n(\gamma_n - \frac{1}{2}\sin 2\gamma_n)} \qquad (12)$$

where γ_n are the roots of the transcendental equation

$$\gamma_n = \frac{R - a}{R} \tan \gamma_n \qquad (13)$$

Equations (12) and (13) permit calculation of concentration gradients throughout the liquid sphere and of the amount of gas diffusing into the gas bubble as a function of time. In order to determine these quantities it is necessary to know the size and distribution of gas bubbles throughout the liquid phase. If the bubbles are uniformly distributed, the liquid volume may be taken to be approximately the total volume of the oil phase divided by the number of bubbles; that is, $1/N = (4/3)\pi R^3$ where N = number of bubbles per unit volume. This establishes the outer radius R of the individual diffusion sphere.

Equations (12) and (13) will be used in the following discussion of the means for establishing the size of the individual gas bubbles.

NONEQUILIBRIUM DURING PRESSURE DECLINE

The final objective of this paper is the development of an analytical method for predicting the nonequilibrium behavior of a typical reservoir undergoing pressure decline. Specifically, this requires determination of the average amount of supersaturation and of the total number of gas bubbles present at any given time during the depletion process. As implied at the outset, the present work is powerless to predict the detailed manner in which the isolated bubbles expand and join to form a connected gas phase capable of transmitting flow of gas.

Method of Calculation

Pressure decline, bubble formation, and diffusion occur simultaneously during the formation of the gas phase in a reservoir which is being depleted. It is the purpose here to describe this interaction approximately by numerical calculations. Because of the complexity of the calculations, it is necessary to approximate this actual condition by assuming, for the purpose of the calculation only, that depletion occurs in steps and that during each step (1) pressure decline, (2) bubble formation, and (3) diffusion occur consecutively rather than simultaneously. That is, in a given time interval pressure is allowed to decline, increasing the supersaturation. During this interval the total number of new bubbles formed may be determined. Following this, from a knowledge of the distribution of bubbles one may then compute how much gas diffuses from the oil into the gas bubbles. The calculation is then repeated.

The distribution of gas and oil during the early stages of development of the gas phase is that of spherical gas bubbles surrounded by oil. It is convenient to reduce this, for purposes of the calculation, to a system consisting of only one bubble surrounded by a spherical shell of its associated oil. The volume of this system, the bubble plus its surrounding shell of oil, is set equal to the reciprocal of the number of bubbles per unit volume of rock. Now, because bubbles are continually forming and growing, this volume changes with time. However, in order to make use of the diffusion equation, the approximation must be made that this volume does not change with time. Over short intervals of time this approximation is reasonable.

Another necessary approximation is that at the beginning of a step the bubble-point pressure of the oil surrounding the bubble is uniform and equal to the average bubble-point pressure. Because of prior diffusion of gas, the bubble-point pressure is not quite uniform; it increases in the case of an old bubble, as the distance from the bubble increases. On the other hand, because bubbles are formed where the bubble-point pressure is the greatest, the bubble-point pressure decreases as the distance from a new bubble increases. Furthermore, the growth of the gas bubble acts to minimize the bubble-point pressure gradient. These factors will tend to cancel when averaged over many bubbles of different ages, and so this approximation should not invalidate the results of the diffusion calculations.

The detailed calculation is made in the following way. A suitable time interval is chosen, and an average radius a of the developed gas bubbles is assumed. The following three calculations are then made and repeated in sequence over the length of time of interest.

1. The supersaturation existing during a given step is taken to be the difference between the average bubble point pres-

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*Although, strictly, one should consider the individual diffusion of each component of the rather complex crude oil, one is forced by lack of computing facilities and adequate theoretical development to consider that the system is composed of a single gaseous constituent and a nonvolatile oil.

sure at the start of the step and the average hydrostatic pressure at the end of the step. The average bubble-point pressure is known from the results obtained in the preceding step; whereas the hydrostatic pressure is obtained from the known, or assumed, pressure history of the reservoir.

2. After the supersaturation existing during a step is calculated, the number of bubbles formed is determined. This number is the product of the rate of bubble formation and the length of time involved in the step. This, of course, requires knowledge of the rate of bubble formation as a function of supersaturation. A running total is kept on the number of bubbles present.

3. The final calculation involved in a given step is the determination of the average bubble-point pressure existing at the end of the step. This is obtained from Equation (12).

The results of these calculations give a history of bubble formation and supersaturation for the conditions chosen. These results are then used as described below to obtain a check on a, the average bubble radius chosen.

The bubble radius a increases with time and also varies from bubble to bubble because the bubbles differ in age. As a first approximation, however, it can be assumed that a single value of the radius may be used in the foregoing calculations. This value of a is calculated by use of the equation developed by Epstein and Plesset (*2*):

$$a = [\gamma + (1 + \gamma^2)^{1/2}](4\pi D_e \gamma^2 t)^{1/2} \quad (14)$$

where

$$\gamma^2 = (C - C_h)/2\pi\rho$$

In order to use Equation (14), $(C - C_h)/\rho$ is expressed in terms of β, p, and p_h. Then an average value for a is calculated by means of the average values of p, p_h, and t found in the previous calculation to exist during the period in which bubbles were forming. This calculated value of a is then used to recalculate the supersaturation and bubble-formation history. After this the radius is once again calculated, and, if necessary, it is used for still another bubble-formation calculation. This iteration is continued until the calculation is consistent. Fortunately the value of a calculated using the results of a bubble-formation calculation is almost independent of the estimated value of a, as can be seen from the following results obtained by use of p_i = 1,000 lb./sq. in. abs., $D_e = 5 \times 10^{-3}$ sq. ft./day and dp_h/dt = 1 lb./(sq. in.) (day).

a_{est}, ft.	a_{calcd}, ft.	Bubbles/cu. ft.
0.100	0.017	8
0.020	0.020	75
0.010	0.022	160
0.001	0.026	1,700

These typical results show, however, that the number of bubbles is extremely sensitive to the value of a used. Because of the approximations involved, it is doubtful whether any physical significance should be attached to the value of a determined in this manner. Nevertheless, it can be considered as a parameter which, when chosen in the above manner, makes the bubble-formation calculations self-consistent.

Results

The calculation technique described above has been employed to determine the nonequilibrium-presure-depletion history for a typical petroleum reservoir. Figure 4 shows supersaturation, bubble-formation rate, and cumulative bubbles formed per cubic foot of reservoir as a function of time for a system undergoing pressure depletion at the rate of 1 lb./(sq. in.)(day). The results show the characteristic behavior for all such systems, viz, formation of most of the bubbles during a relatively short period of time and a continually declining supersaturation after the maximum is achieved. These computations were made by using the Rangely data and an effective diffusion coefficient of $D_e = 5 \times 10^{-3}$ sq. ft./day. The time interval chosen was 1 day. Recalculation with the interval of ½ day gives results which are indistinguishable from those shown in Figure 4. This is considered a satisfactory indication that the step procedure leads to reasonably correct results.

The foregoing calculations relied upon the extrapolation of the Rangely bubble-formation-rate data described earlier. Nevertheless, further computation showed that the results of the calculations, in terms of total bubbles formed and supersaturation history, were almost independent of the method of extrapolation of the data at low rates of bubble formation. In fact, moderate or large changes in any of the variables involved does not cause any significant change in the results. For this reason it is felt that reasonable confidence can be placed in this method of performance calculation. This, of course, does not mean that it would not be desirable to have more experimental information regarding effect of supersaturation on bubble-formation rates and variation of diffusion coefficients with temperature, pressure, and composition.

Additional calculations covering the whole range of pressure-decline rates of interest in both the reservoir and the laboratory have also been made. These calculations were based upon a diffusion coefficient, D_e, of 5×10^{-3} sq. ft./day and a gas solubility, β, of 0.05 std. cu. ft. gas/(cu. ft. oil)(lb./sq. in. bubble-point pressure). In all cases the results were similar to those shown in Figure 4.

The results of these comprehensive calculations are summarized in Figures 5 and 6. Figure 5 shows the maximum supersaturation attained during pressure depletion as a function of the rate of pressure decline. Included for comparison is the behavior assumed by Kennedy and Olson (*6*). On the basis of the information shown in Figure 5, there is no reason to expect supersaturation to have a significant effect upon reservoir engineering calculations except perhaps at high pressure-decline rates attainable only in the laboratory.

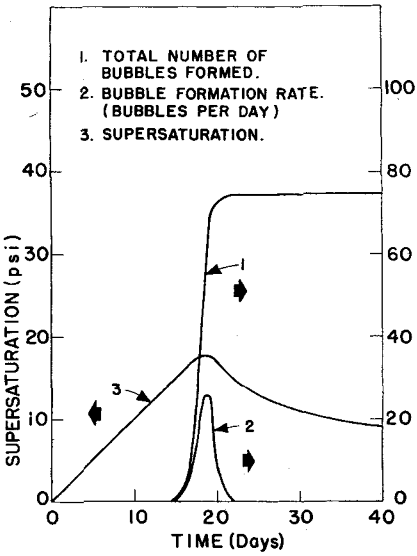

Fig. 4. Calculated nonequilibrium history for a typical oil reservoir undergoing depletion at a rate of 1 lb./(sq. in.) (day).

The hydrostatic pressure existing during the period of bubble formation affects the size of the bubbles according to Equation (14). This results in the hydrostatic pressure having an effect on the supersaturation. As can be seen in Figure 5, this effect is quite small at reservoir rates of pressure decline but becomes large at laboratory rates.

The nonequilibrium calculations described above yield information as to the number of bubbles formed as well as the supersaturations reached. This information has been shown to be of great importance in connection with the performance of limestone-type reservoirs (*9*). Figure 6 presents a summary of the results obtained for the total number of bubbles formed as a function of the pressure-decline rate. As before, Kennedy and Olson's results are included for comparison. Here it is seen that the hydrostatic pressure has a marked effect upon the number of bubbles formed. The most useful conclusion which can at present be obtained from the results shown in Figure 6 is that, other things being equal, increasing the rate of pressure decline by a factor of ten results in the formation of about ten times as many bubbles.

The method of calculation described above is not limited to constant rates of pressure decline. However, each case of a changing decline rate must be treated individually; that is, no general curves such as those shown in Figures 5 and 6 can be drawn to cover these cases. In most oil-field operations the rate of pressure decline changes so slowly that a constant decline rate can be assumed to exist during the period of bubble formation. This is not true, however, of most laboratory solution gas drives. Thus, for the majority of field applications the results presented in Figures 5 and 6 will suffice to indicate the general behavior to be expected, while for each laboratory application, an individual calculation as outlined above will probably be required. In either event the analysis given here of the nonequilibrium development of a gas phase during pressure-decline operations is believed to be adequate at present for most engineering and laboratory investigations.

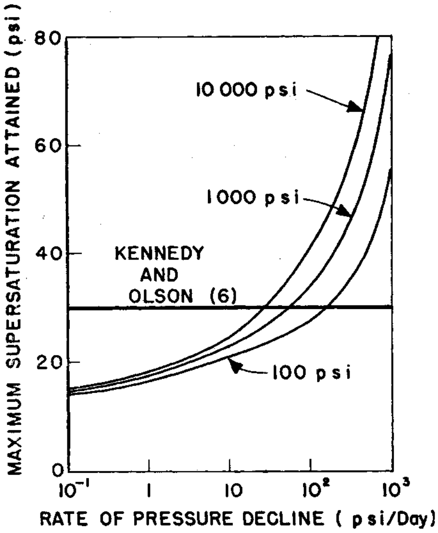

Fig. 5. Calculated maximum attainable supersaturation for systems undergoing pressure decline at constant rate.

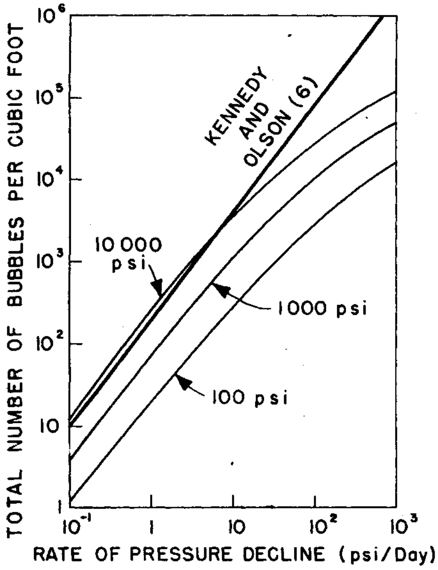

Fig. 6. Calculated total number of bubbles formed per cubic foot in systems undergoing pressure decline at constant rate.

CONCLUSIONS

Bubble formation in quiescent liquids is erratic. However theoretical considerations predict that nucleation times may be described by a simple, exponential probability-distribution function. This has been confirmed by experiment.

The mean rate of bubble formation increases extremely rapidly with increasing supersaturation. In the analysis of reservoir-depletion performance, this effect greatly overshadows the dependence on fluid composition.

Calculations were made of the nonequilibrium behavior of petroleum reservoirs. At normal rates of pressure decline, it was found that the assumption of equilibrium between the oil and gas phases is satisfactory for the purpose of determining fluid properties.

The method of this paper may be used to predict the total number of bubbles formed under a given set of conditions. Calculations show that the high rates of pressure decline normally used in the laboratory result in the formation of considerably greater concentration of bubbles than would be expected under field conditions. This must be considered in the interpretation of laboratory solution-gas-drive tests, since other workers have shown that in certain types of porous media the amount of oil recovered by depletion is sensitive to the number of bubbles formed.

NOTATION

A = cross-sectional area normal to the concentration gradient, sq. ft.
a = bubble radius, ft.
C = dissolved gas concentration at the bubble-point pressure, p, std. cu. ft./cu. ft. oil
C_h = dissolved gas concentration at the hydrostatic pressure, p_h, std. cu. ft. gas/cu. ft. oil
c = dissolved gas concentration, std. cu. ft. gas/cu. ft. oil
D_e = effective diffusion coefficient, sq. ft./day.
J = rate of bubble formation, bubbles/(day)(cu. ft. solution)
J_t = true rate of bubble formation, bubbles/(day)(volume studied)
J_0 = observed rate of bubble formation, bubbles/(day)(volume studied)
M_r = mass rate of transfer, st. cu. ft. gas/day
$N = (4/3\pi R^3)^{-1}$ = bubbles/cu. ft.
n = number of statistically identical runs
$P(t_1, t_2)$ = probability of bubble formation occurring in the time interval t_1 to t_2
p = bubble-point pressure, lb./sq. in.
$\bar{p}$ = average bubble-point pressure, lb./sq. in.
p_h = hydrostatic pressure, lb./sq. in.
p_i = initial bubble-point pressure = initial hydrostatic pressure, lb./sq. in.
p' = probability of bubble formation occurring in a unit of time, Δt
$q = (1 - p')$ = probability of bubble formation not occurring in a unit of time, Δt
r = radius to any point within a spherical shell of oil surrounding a gas bubble, ft.
R = radius to outer boundary of the spherical shell of oil surrounding the gas bubble, ft.
t = time, days
$\bar{t}$ = mean time required for bubble formation, days
t_x = time required for bubble formation in x out of n runs, days
Δt = a unit of time, day
x = number of runs in which bubble formation occurred by time t_x
α = probability density function parameter, day^{-1}
β = gas solubility coefficient, std. cu. ft. gas/cu. ft. oil/(lb.)(sq. in. bubble-point pressure)
γ_n = nth root of the equation, $\gamma_n = R - a/R \tan \gamma_n$
σ = standard deviation, day
σ^2 = variance, day^2
Φ = probability density function governing first bubble formation

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