[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Measurement of Foam Stability[1a]

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A multiplicity of methods is in use for determining the foaming of liquids, aqueous and nonaqueous. In general, they were developed to provide an answer to specific problems encountered in industrial practice, and they have not been completely correlated or analyzed.

The present paper is an attempt to show how far the stability of foams may be determined, independent of the particular method of measurement. The theory of foam measurement is analyzed, and the factors are estimated which operate to make one foam differ from another.

It will be shown that to a very great extent all the methods of foam measurement yield similar information as to the factors involved. In a few cases the characteristics of the foam may depend upon its mode of formation. For example, in certain non-aqueous foams formed by reducing the pressure, the froths initially formed are stable until they are stretched too far by further evacuation, whereupon they collapse. Certain foams in which the foaming agent produces a surface film of high viscosity likewise need further study.

The writers have been engaged in the study of a foaming problem sponsored and supported by the National Advisory Committee for Aeronautics at Stanford University and supervised by Professor J. W. McBain, and they have made use of the extensive experience obtained during those investigations as well as of the data of previous publications and the literature.

Part I

Data for Different Types of Foams.—Foams may be very different according to the manner in which they are formed. They may be made very wet, as by incomplete beating, or by putting in insufficient gas, or they may be dried by further input of gas or by stretching or by drainage; they may be studied at any of these stages. Aleinikov[1c] introduced the somewhat arbitrary distinction, which designates as dynamic methods those in which observations are made during formation of the foam, and as static methods those in which the foam is formed before observations are begun.

In 1936 Bikerman[2] proposed a unit of foaminess for wet dynamic foams, and again in 1941 essentially the same unit was proposed by Hoffmann and Peters.[3] This unit cannot have the general significance ascribed to it by Bikerman, *i. e.*, the average lifetime of a bubble in the foam; it does, however, measure the average time that gas remains entrained in the foam. Generalizing the concept to apply to all types of foam measurement, Ross[4] proposed the units L_l and L_g, measuring respectively the *average* lifetimes in minutes of liquid and gas in the foam.

$$L_l = 1/l_0 \int_0^{l_0} t\,dl \qquad (1)^{4a}$$

$$L_g = 1/g_0 \int_0^{g_0} t\,dg \qquad (2)^{4a}$$

where g and l refer to the volumes of gas and liquid at time t, the original volumes being g_0 and l_0. For example, if drainage of liquid were strictly linear with time, the liquid would all be gone at $2L_l$.

In the case of dynamic foams L_g is measured by the methods described by Bikerman[2] and Hoffmann and Peters[3]; for static foams both L_l and L_g can be measured either by graphical or analytical methods. It is frequently desired, if possible, to express foam stability as a single number for the purpose of comparing members of a series of samples. A direct comparison of foam stabilities may be made by use of the concept L_f the average lifetime of the foam in minutes.

$$L_f = 1/f_0 \int_0^{f_0} t\,df = 1/f_0 \int_0^{T} f\,dt = \frac{1}{(l_0 + g_0)} \int_0^{T} l\,dt + \frac{1}{(l_0 + g_0)} \int_0^{T} g\,dt \qquad (3)$$

where f is the total volume of foam ($f = l + g$) at time t and T is the time for total collapse of the foam. This unit is related to L_l and L_g by the introduction of another concept, the relative foam density, defined as

$$d = l/f = l/(l + g) \qquad (4)$$

L_f can then be calculated from the equation

$$L_f = L_g + d_0(L_l - L_g) \text{ or } (g_0 + l_0)L_f = g_0L_g + l_0L_l \qquad (5)$$

where d_0 is the initial foam density. Equation (5) is readily derived from equations (3) and (4). L_f is always intermediate in value between L_g and L_l.

The resolution of a single value of L_f into two values, L_l and L_g, provides more detailed information concerning the nature of the foam. The concurrent phenomena of drainage and film rupture occur during the existence of every foam.

[1a] Presented before the Division of Colloid Chemistry at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April 6, 1944, Abstracts, Section E, page 6.

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[1c] N. A. Aleinikov, *Kolloid Beihefte*, **36**, 82 (1932).

[2] J. J. Bikerman, *Trans. Faraday Soc.*, **34**, 634 (1938).

[3] K. Hoffmann and H. Peters, *Kolloid-Z.*, **97**, 161 (1941).

[4] S. Ross, *J. Phys. Chem.*, **47**, 266 (1943).

[4a] It is frequently more convenient in practice to express these integrals in an equivalent form. Since the curves terminate on both axes, then $\int_0^{l_0} t\,dl = \int_0^{T} l\,dt$, where T = time for total collapse of the foam.

Some idea of their relative importance in the case of any foam is obtained by a comparison of the values L_l and L_g. If drainage is a more pronounced factor than film rupture, as is normally the case with a freshly formed and therefore wet foam, then liquid is removed from the foam at a faster rate than gas is liberated. Consequently L_g will be greater than L_l. If, on the other hand, film rupture or coalescence of bubbles at the exposed surface of the foam takes place before drainage of the underlying films has had time to assert itself, then the gas is liberated from the foam more rapidly than the liquid. This happens frequently in the presence of an antifoaming agent, capable of destroying relatively thick films before they have time to drain. Here L_g is smaller than L_l. It is consequently extremely informative in the case of any single foam to have values of both L_l and L_g. Some advantages of employing these units will be demonstrated later.

Methods of Measurement.—Methods of measuring foam have already received extensive discussion.[5] In general the nature of the substance being investigated determines the manner in which the foam is best produced, liquids of slight foam forming ability requiring more vigorous treatment, such as whipping. Bubbling a gas through the liquid is a milder treatment, better suited for liquids of greater foam-forming ability but with certain liquids it may produce a much larger volume of foam.

Many of the present experiments were done on hydrocarbon oils, liquids of relatively slight foaminess. Both beating and bubbling were used to obtain foams at room temperature, the latter technique also being extended to production of foams at elevated temperatures. Fig. 1 is a schematic diagram of a "static" foam meter in which the foam is created by bubbling gas through the liquid. In the laboratory three foam meters of this type were constructed, differing in the dimensions of the apparatus as well as in the type and porosity of the gas dispersing bubbler. The "static" apparatus is similar to many "dynamic" foam meters that have been described previously,[2,6,7,8] but with the addition of a glass jacket enclosing the vertical foam cylinder. This jacket terminates in a bulb at one end and has a reflux condenser attached to the other. Liquids of suitable boiling point are heated in the bulb and the vapors are condensed and refluxed, providing a constant elevated temperature in the foam cylinder. The following liquids are used to provide a temperature range from 46 to 117°: carbon disulfide, 46°; acetone, 56°; methyl alcohol, 65°; 95% ethyl alcohol, 78°; water, 100°; and *n*-butyl alcohol, 117°.

The amount of sample taken depends on the dimensions of the foam cylinder, enough being taken to cover the porous bubbler but not enough to prevent all the liquid from being brought into the foam. Although values of L_l and L_g depend both on the amount of liquid originally present in the foam and on the dimensions of the apparatus, it will be shown later that a conversion can be effected into a value independent both of the initial volume of liquid used and the dimensions of the apparatus.

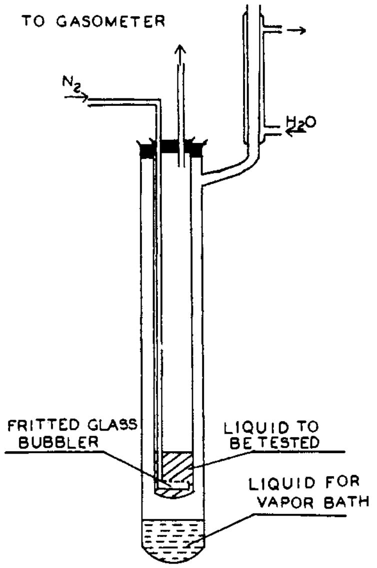

Fig. 1.—Bubbler type foam meter.

Nitrogen gas flowing at a constant pressure (and previously dried over calcium chloride for use with non-aqueous liquids), is introduced through a porous ceramic bubbler or through a sintered glass membrane. The bubbling is continued for about five minutes after all the liquid is in the form of a froth. The effect of variations in the rate of flow of the nitrogen gas was investigated, measuring the rate at which gas is displaced by the foam to obtain the rate of gas input. Any rate of gas flow within the limits where production of a suitable amount of homogeneous foam is possible yields results that are reproducible and in agreement. Thus, for example, rates of flow of 15 cc./minute and 75 cc./minute are not too far apart for concordant results. After some experience it is no longer deemed necessary to measure the rate of gas flow for each experiment; a constant pressure device keeps automatically the rate of flow well within the proper limits for reproducibility. After a homogeneous foam is obtained, the nitrogen is shut off and the foam/air and foam/liquid interfaces recorded as drainage and collapse proceed.

The production of foam by means of beating is also used. Two hundred grams of the liquid is stirred at the top speed of a Sunbeam Mixmaster for three minutes and then poured quickly into a 500 ml. graduated cylinder. The collapse of the foam is observed at suitable intervals just as in

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(5) S. Ross, *Ind. Eng. Chem., Anal. Ed.*, **15**, 329 (1943).

(6) E. L. Lederer, *Seifensieder-Ztg.*, **63**, 331 (1936).

(7) C. W. Foulk and J. N. Miller, *Ind. Eng. Chem.*, **23**, 1283 (1931).

(8) G. L. Clark and S. Ross, *ibid.*, **32**, 1594 (1940).

TABLE I

FOAM STABILITIES (AVERAGE LIFETIMES IN MINUTES OF FOAM, LIQUID AND GAS, RESPECTIVELY, IN THE FOAM) OF HYDROCARBON OILS AT DIFFERENT TEMPERATURES BY BUBBLING METHOD

Temp., °C.	Oil A			Oil B			Oil C			White Oil 1			White Oil 2			White Oil 3		
	L_f	L_l	L_g	L_f	L_g	L_l	L_f	L_l	L_g	L_f	L_l	L_g	L_f	L_l	L_g	L_f	L_l	L_g
26	29.5	18.3	32							6.8	5.7	7.1	4.0	3.9	4.1	1.0	0.95	1.0
46				16.5	9.8	17.5	1.9	2.3	1.8				1.14	1.06	1.16	0.3	.3	0.3
56	6.9	5.3	7.2	10.0	6.4	10.5	4.0	4.0	4.0	1.2	1.05	1.2	0.66	0.61	0.67			
64.5													.39	.29	.43			
78	2.9	2.3	3.0	3.2	2.3	3.4	2.0	2.0	2.0	0.47								
100	1.10	0.86	1.15	1.7	1.25	1.8	1.0	1.0	1.0									
117				0.8	0.8	1.1												

the bubbling method. This method was employed only at room temperature, 26°. In some cases, beating cuts down a previously formed voluminous foam to a much smaller value, equal to that produced by direct beating of the same liquid. Hence volume of foam and foam stability are not always directly related qantities.

In every case of a static foam where values of L_f, L_g and L_l are desired, it is necessary to observe the variation with time of the foam–liquid and the foam–gas interface. To obtain L_g the volume of gas in the foam is plotted against the time; the area under the resulting curve is obtained by graphical methods. To obtain L_l the same procedure is followed, using the volume of liquid in the foam. By this method it is not necessary to know the mathematical equation that expresses either drainage or rupture of the films. In some cases however it is observed that a linear or an exponential relation holds and the integration can be readily performed mathematically without the necessity of taking many data or plotting the experimental points. In any case where drainage or film rupture is linear with time the value of L_l or L_g is, of course, one half of the intercept on the time axis.

Materials

The most extensive experiments here reported were conducted on six hydrocarbon oils. Oils A, B and C are SAE 60 engine lubricating oils of different origin. They are selected as different types from a larger body of experiments; oils A and B are examples of those oils most commonly encountered and oil C is one of a smaller group exhibiting different foaming behavior. White oils 1, 2 and 3 are medicinal grade paraffin oils of different origin. Measured in Saybolt seconds the viscosities of the latter are, respectively, 166, 106 and 59 at 130°F. (54.4°C.).

Experiments were also conducted on a 2% solution of "Aerosol OT" (sodium diisooctyl sulfosuccinate) in triethanolamine, as an example of a non-aqueous foaming system. A few experiments on beer, as an example of an aqueous foaming system, are also included.

Results

Table I gives the values of L_f, L_g and L_l for all the samples selected both at room and at elevated temperatures, using the bubbling apparatus. Table II gives L_f, L_g and L_l for oils A, B and C by the beating method, and for 2% Aerosol OT in triethanolamine at 100° and beer at 25° by the bubbling method. When values of L_f are below about 0.3 minute the bubbling foam meter is no longer suitable for taking measurements. For this reason the white oils are investigated only in the lower temperature range.

TABLE II

A. FOAM STABILITY OF ENGINE LUBRICATING OILS AT 26° BY BEATING METHOD

	L_f	L_l	L_g
Oil A	64.1	45.2	79.2
Oil B	85.9	58.9	103.6
Oil C	28.4	29.7	27.3

B. FOAM STABILITY OF OTHER SYSTEMS BY BUBBLING METHOD

System	Temp., °C.	L_f	L_l	L_g
2% Aerosol OT solution in triethanolamine	100	87.6	85.6	88.8
Beer	25		4	30

The data, from which those diagrams and other results quoted in this paper are obtained, are available as a Bibliofilm Supplement.[9] These data are only part of a much more extensive series of experiments, the results of which are further drawn upon in Figs. 5 and 6. It is not considered necessary, however, to make all the data available *in extenso*.

Discussion

Figures 2, 3 and 4 are typical decay curves for both the gas and the liquid in the foam. Figure 2 is from data obtained by the bubbling method. The rate of escape of gas from the foam is linear over a large portion of the curve. This has been found to be the case in a large number of experiments with different oils, especially at the higher temperatures. Figure 3, on the other hand, representing the decay curves for the same oil by the beating method, shows an initial period of very slow gas escape before the linear portion of the curve appears. Foams obtained by beating as specified in the method are very much denser than

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(9) This supplement can be obtained as an American Documentation Institute Document from American Documentation Institute, Science Service Building, 1719 G Street, N.W., Washington, D. C., remitting $0.50 for microfilm or $0.50 for photoprints.

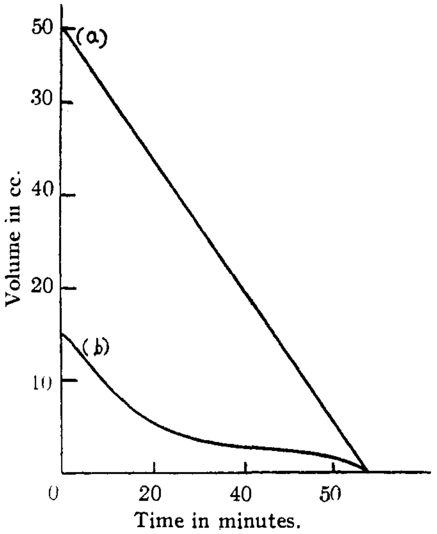

Fig. 2.—Decay curves for oil A at 26°, bubbling method: (a) decay curve for gas in foam; (b) decay curve for liquid in foam.

those obtained by bubbling, the air being entrained in the excess liquid in the form of an "emulsion." The initial flatter portion of the curve may therefore be attributed to an initial drainage or "creaming" of the fine air bubbles before any appreciable film rupture can take place. Figure 4, representing the decay curves for a 2% solution of Aerosol OT in triethanolamine at 100° by the bubbling method, illustrates a case where rupture of the films begins at once; the decay curves are not linear but concave. The values of L_f, L_l and L_g are very closely alike.

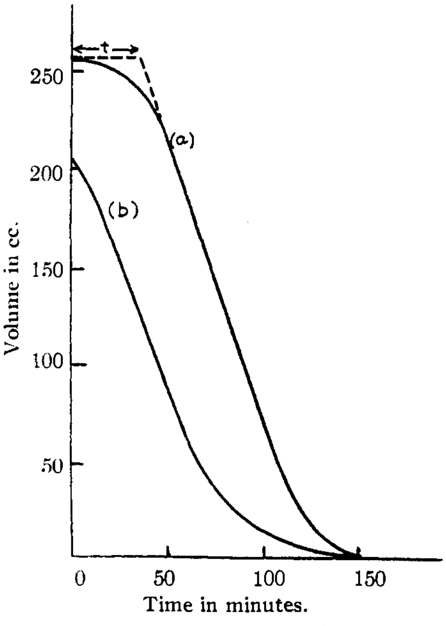

Fig. 3.—Decay curves for oil A at 26°, beating method: (a) gas in foam; (b) liquid in foam.

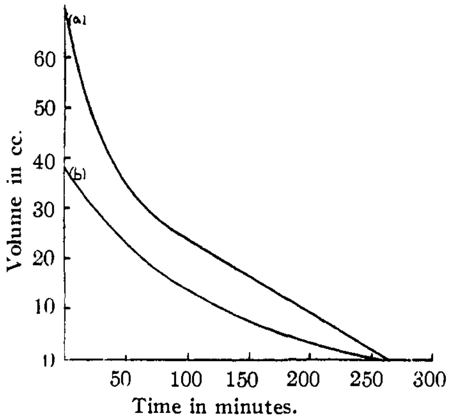

Fig. 4.—Decay curves for 2% Aerosol OT in triethanolamine at 100°, bubbling method: (a) gas in foam; (b) liquid in foam.

A comparison of L_l and L_g values is frequently informative concerning the nature of the foam that has been observed. For example, in the case of the 2% solution of Aerosol OT in triethanolamine at 100°, gas and liquid in this foam are present, on the average, for equal periods of time.

Another example is the behavior of Oil C which has considerably lower values of L_l and L_g at lower temperatures when compared with the other oils of the same viscosity. It is noteworthy that between 46 and 56° there is a sharp break in the foaming characteristics of Oil C, and the foam stability *increases* in that temperature range. Also unlike the other oils the value of L_l is greater than the value of L_g below 56°. This case illustrates the presence of an antifoaming agent that makes the liquid films less stable and allows the gas to escape more rapidly. As relatively thick films are breaking, larger amounts of liquid are still present in the foam when the rupture of the films takes place. Apparently the agent is no longer operative above about 50°. Above 56° the values of L_l and L_g approach each other and also become more nearly like the other oils. A phenomenon of another nature is shown by the other oils and to an even more marked extent by the foam obtained from beer. Here the values of L_g are all greater than those of L_l, by several fold in the case of beer. This is to be interpreted as drainage in the films to very thin laminae before ultimate rupture takes place the gas being held in the foam for a long period of time while most of the liquid drains away.

Part II. Further Analysis of the Factors in Characterizing Foam Stability

Preliminary Mathematical Formulation.—It has proved a useful concept that many liquid films attenuate by draining out of liquid to a critical thickness at which they are no longer capable of stable existence. In cases where spontaneous film rupture takes place it is difficult to find any other mechanism. An approximate theoretical derivation of L_l and L_g can be obtained by employing this idea. The application of Poiseuille's law to the drainage of liquid from between vertical immobile planes results in the equation for the volume rate of drainage of liquid in the film.

$$-\mathrm{d}l/\mathrm{d}t = bG\delta^3\rho/12\eta \qquad (6)$$

where b = horizontal dimension (large compared to δ); δ = thickness of film; ρ = density of liquid; G = gravitational constant; η = viscosity of liquid; and l = volume of liquid in the film.

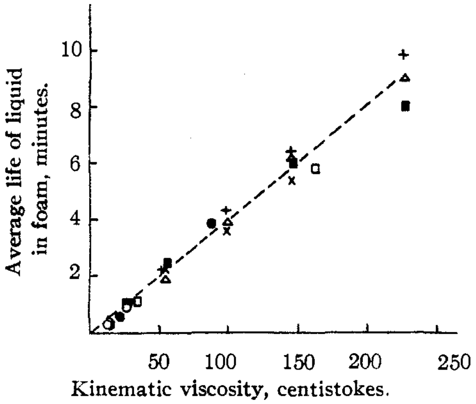

Fig. 5.—Average life of liquid in foam *vs.* kinematic viscosity: □, white oil 1; ●, white oil 2; ○, white oil 3; ×, lub. oil A; +, lub. oil B; △, lub. oil D; ■, lub. oil E.

If the thinning remains of constant vertical and horizontal dimensions, a and b, during drainage

$$l = ab\delta \qquad (7)$$

$$\mathrm{d}l/\mathrm{d}t = ab(\mathrm{d}\delta/\mathrm{d}t) \qquad (8)$$

Substituting equations (7) and (8) in (6)

$$-\mathrm{d}l/\mathrm{d}t = Gl^3\rho/(12\eta b^2a^3) \qquad (9)$$

The idea of limiting dimensions of the liquid film is now introduced to terminate the existence of the film after a time T. At time T the limiting volume of liquid in the film, l_T, is the lower limit for the integration to obtain L_l for this film.

$$L_l = 1/l_0 \int_{l_T}^{l_0} t\,\mathrm{d}l = 1/l_0 \int_0^T l\,\mathrm{d}t = \frac{12\eta b^2a^3}{\rho G l_0}(1/l_T - 1/l_0) \qquad (10)$$

Expressing $l_T/l_0 = \alpha$ and recalling that $l_0 = ab\delta_0$, then

$$L_l = (12\eta a/\rho G\delta_0^2)(1-\alpha)/\alpha \qquad (11)^{10}$$

If the liquid film is part of an idealized foam then its final collapse, after a time T, will release the volume of gas enclosed. Therefore $L_g = T$. By integration of equation (4) to obtain T, the time for total collapse

$$L_g = \frac{6\eta a}{\rho G\delta_0^2}\left(\frac{1-\alpha^2}{\alpha^2}\right) \qquad (12)^{10}$$

$$L_l/L_g = 2\alpha/(1+\alpha) \qquad (13)^{10}$$

Equations (11) and (12) above, although highly idealized, are nevertheless of value in their indication of the influence of various factors on the foam stability. The influences of gravity and density are immediately obvious even without the mathematical formulation. The influence of viscosity requires more extended mention.

The Linear Influence of Viscosity on the Life of Foam.—Speculations on the influence of viscosity on foam stability are frequent in the literature although the present authors are not aware of any extensive experimental results Equations (11) and (12) predicate a linear relation between foam stability and viscosity, all other factors being constant.

In order to demonstrate experimentally the linear relation, the kinematic viscosity of lubricating and white oils was determined throughout a temperature range of 26 to 117° by means of a Saybolt Universal Viscometer. Conversion of the results from Saybolt Seconds to centistokes was made following ASTM Tables D446-39. In Fig. 5 values of L_l at different temperatures, determined by the bubbler method, are plotted against the corresponding viscosity. Oil C is omitted from the figure because of its abnormal character. From Fig. 5 it is evident that the viscosity is the primary factor influencing the life of the liquid in the foam for these homologous substances, since all points lie within a few per cent. of the dotted line, although definite secondary tendencies are noticeable. These secondary tendencies are more pronounced in the variation of L_g with viscosity as shown in Fig. 6. In this case the oils fall into groups; oil B forms the most stable foams, oils A and D fall in an intermediate classification and another oil E and the white oils form the least stable foams. As is the case with L_l, within each group the viscosity bears a linear relation to L_g.

Further confirmation of the linear relation of viscosity and foaminess is found in an aqueous system. The data of Helm[11] on the foam stability of beer at different temperatures have been recalculated by Ross and Clark.[12] The unit designated Σ in that paper is in this case equal to L_l. A comparison is made with the viscosity of water at corresponding temperatures in Table III. The ratio of L_l to η is constant within the limits of accuracy of the data.

TABLE III

THE EFFECT OF VISCOSITY ON THE AVERAGE LIFE OF LIQUID IN THE FOAM, L_l, FOR PASTEURIZED BEER

Temp., °C.	L_l in minutes	Viscosity of water at corresponding temperature,[a] centipoises	Ratio L_l/η
10	4.1	1.31	3.1
15	3.6	1.145	3.1
20	3.35	1.01	3.3

[a] "International Critical Tables," 5, 10 (1939).

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(10) These equations can also be obtained by integration of equa-on (11) of ref. 4.

(11) E. Helm, *Wochschr. Brau.*, **50**, 241 (1933).

(12) S. Ross and G. L. Clark, *Wallerstein Labs. Commun. Sci. Practice Brewing*, No. 6, 46 (1939).

Foam Density.—In Fig. 6 the splitting of the oils into definite groups is evidence that a factor other than viscosity is also serving to influence the foam stability. The possible factors that remain, according to equations 11 and 12, are h, the foam height (corresponding to a), δ_0, the initial film thickness; and α, the ratio of the final to initial amounts of liquid in the foam. The first factor, though important when comparing different methods of foam measurement, is in this case relatively minor; if it is taken into account the curves of Figure 6 are more nearly straight lines, the difference in slope not materially altered. The second factor is a function of the initial foam density and bubble size which are approximately equal for all the foams of Figs. 5 and 6, thus eliminating this factor. The influence of α, the effect of drainage of the foam, is therefore clearly indicated, oil B having the lowest value of α, oils A and D an intermediate value and oil E and the white oils the highest value. From equations 11 and 12 it can be seen that although changes in α would be reflected in the values of L_l as well as L_g, it exercises a greater influence on the latter value, as it enters in a higher power. This is in accord with the greater differentiation of the oils that is afforded by the use of L_g in Fig. 6, compared to the use of L_l in Fig. 5.

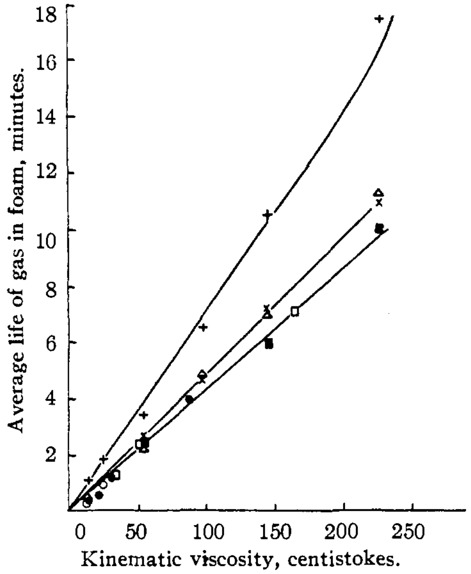

Fig. 6.—Average life of gas in foam *vs.* kinematic viscosity: □, white oil 1; ●, white oil 2; ○, white oil 3; ×, lub. oil A; +, lub. oil B; △, lub. oil D; ■, lub. oil E.

The quantity α is a monotonic function of the foam density at which the films become unstable. During the collapse of any real foam the foam density varies from the top to bottom and also in general with the time as drainage and film rupture proceed. At any given time the average relative foam density throughout the foam column is defined by equation 4, $d = l/(l + g)$. If d is plotted against the volume of liquid in the foam, l, and extrapolated to zero volume, the value obtained, d_T, may be regarded as the final density at which the last remaining films break and hence equal to that relative foam density at which the films become unstable. The quantity d_T is therefore related to α; however, the presence of Gibbs "angles" makes this relation more complex than the simple proportionality calculable from the definition of α in the idealized case of a single vertical film.

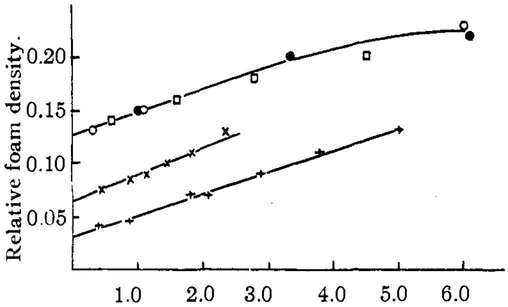

Fig. 7.—Relative foam density *vs.* volume of liquid in foam at 56°: □, white oil 1; ●, white oil 2; ○, white oil 3; ×, lub. oil A; +, lub. oil B.

Figure 7 shows typical curves for the variation of d with l for the oils A and B and the white oils 1, 2 and 3, using the bubbler method. Values of d_T obtained by extrapolation of these curves are in Table IV. For comparison, values of d_T in oils A, B, D and E, from the data obtained by the beating method, are also included. The prediction from the curves of Fig. 6 that the values of L_g and consequently d_T for all the oils would fall into three groups is borne out by the data in Table IV; oil B lowest, oils A and D an intermediate value and E and the white oils the highest value. Values of d_T are also observed to be independent of temperature and the same for both beating and bubbling methods. The probability of the existence of a limiting film thickness δ_T is greatly enhanced by these results.

TABLE IV

VALUES OF LIMITING FOAM DENSITY d_T AT DIFFERENT TEMPERATURES FOR THE OILS OF FIGURE 6

Oil	26°[a]	46°	56°	78°	100°
A	0.08		0.07	0.08	0.07
B	.06	0.02	.03	.05	.05
D	.08	.05	.07	.08	.07
E	.2	.12	.13	.13	
White Oil 1			.13	.13	
White Oil 2		.12	.13		
White Oil 3		.12			

[a] Values in this column from data obtained by beating method; the other temperatures, by bubbling method.

Figure 8 shows the d–V curve for oil C, from the data obtained by beating and bubbling methods. By both methods the same phenomenon is observed; a pronounced hump in the curve, due

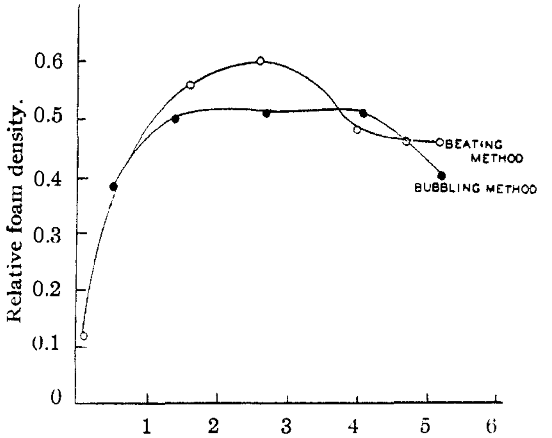

Fig. 8.—Variation of foam density with volume of liquid in foam for oil C at 26°.

to such a rapid collapse of the top films at the beginning that the amount of underlying liquid is greatly increased relative to the remaining amount of enclosed gas.

Influence of the Height of the Foam Column and Generalization of L_g.—Before investigating the influence of the factor a, in equations 11 and 12, it will be advantageous to set up a slightly more sophisticated model for a foam. If the foam column is regarded as a series of vertical films of height A, then equation 12 can be applied to obtain the time required for the top film to rupture; if the initial film thickness is δ_0 and the limiting film thickness is δ_T

$$t_1 = (6\eta A/G\rho)(1/\delta_T^2 - 1/\delta_0^2) \qquad (14)$$

After the top film has broken and the liquid of which it was composed is deposited on the underlying film, the new film exposed will drain and rupture in a time t_2; and each successive film exposed thereafter will require the same time to rupture. An exaggerated collapse curve for such a foam is shown diagrammatically in Fig. 9. From equation (14) the expression for t_2 may be derived

$$t_2 = \frac{6\eta A}{G\rho\delta_T^2}\left(\frac{\beta^2 - 1}{\beta^2}\right) \qquad (15)$$

where

$$\beta = (\delta_T + \delta_2)/\delta_T \qquad (16)$$

and δ_2 is the thickness of the penultimate film at the time of collapse of the top or ultimate film. β should have the value of 2 or greater. From the geometry of Fig. 9

$$L_g = t_1 + \frac{1}{2}(T - t_1) = \frac{1}{2}(T + t_1) = t_1 + \frac{1}{2}(t_2/A)h_0 \qquad (17)$$

where h_0 is the initial foam height and t_1 is the elapsed time before appreciable breakage of foam begins. Substituting equations (14) and (15) in equation (17)

$$L_g = \frac{6\eta A}{G\rho}\left(\frac{1}{\delta_T^2} - \frac{1}{\delta_0^2}\right) + \frac{3\eta h_0}{G\rho\delta_T^2}\left(\frac{\beta^2 - 1}{\beta^2}\right) \qquad (18)$$

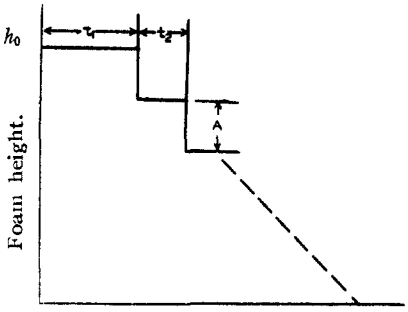

Fig. 9.—Collapse curve for idealized foam.

If the effect of creaming is eliminated (see below) and $A \ll h_0$, the first term in the last equation is negligible; for a given liquid β is a constant; hence equation (18) may be written

$$L_g/\nu h_0 = K\Theta \qquad (19)$$

where $\nu = \eta/\rho$, the kinematic viscosity, and Θ is a complex function of the limiting foam density and K is a numerical constant.

To test the relation some account must be taken of the different nature of the foam produced by different methods. It can be seen from Fig. 3 that a fine dispersion of air in the liquid by whipping produces a foam that requires some time, t_1, for draining of liquid or "creaming" of air before rupture of the films can take place to any extent. The application of equation (19) requires the determination of t_1—the idealized "creaming" time. In any actual foam no sharp discontinuity occurs at t_1 since usually a small amount of film rupture takes place even during the initial "creaming" period. The real curves are therefore idealized, as illustrated by the dotted lines of Fig. 3. A re-definition as L_g', based only on the idealized curve starting at t_1, is necessary if the data are to be used in equation (19). When the foam is produced in the bubbling type of foam meter, there is no period of "creaming" for the foams here investigated. Consequently idealization and recalculation of these data are not required.

A comparison of the values of $L_g/\nu h_0$ and $L_g'/\nu h_0$ for oils A and B, using different types of foam meter is given in Table V. The agreement in the values obtained justifies the procedure for the idealizing of the experimental curve in the case of the beating type foam meter.

Data at different temperatures are also included in Table V. Since it has already been shown experimentally that d_T is independent of the temperature, an experimental test of equation (19) would be to obtain $L_g/\nu h_0$ also independent of temperature for any given substance. This is indeed shown to be the case in the last column of Table V. Thus the average life of the gas in the foam, L_g, is proportional to the kinematic viscosity and to the height of the foam column. The proportionality constant is independent of temperature, the dimensions of the apparatus and the amount of liquid charged, and is the same whether a beating or a bubbling method is used.

For comparison, some values of L_g/ν are included in Table V. They are found to be approximately constant only for a given apparatus containing a fixed amount of oil (h_0 nearly unchanged).

TABLE V

Test method	Temp., °C.	ν, c.s.	L_g, min.	h_0, cm.	$L_g/\nu \times 10^3$	$L_g/\nu h_0 \times 10^3$
		Oil A				
Beating (46 mm. tube)	26	1085	50.5	28.6		1.62
Bubbling (18 mm. tube)	26	1085	33	19.3	30.2	1.57
Bubbling (18 mm. tube)	56	145	7.2	31.3	49.6	1.59
Bubbling (18 mm. tube)	78	55	3.0	32.8	54.5	1.64
Bubbling (18 mm. tube)	100	26	1.2	30	46	1.54
Bubbling (18 mm. tube)	100	26	1.75	45		1.50
Bubbling (28 mm. tube)[a]	100	26	2.0	48		1.57
		Oil B				
Beating (46 mm. tube)	26	1085	61.3	29.9		1.90
Bubbling (18 mm. tube)	46	227	17.5	39	77	1.98
Bubbling (18 mm. tube)	56	145	10.5	39.5	72.5	1.93
Bubbling (18 mm. tube)	64.5	98	6.5	33	66	2.00
Bubbling (18 mm. tube)	78	55	3.4	30	62	2.05
Bubbling (18 mm. tube)	100	26	1.8	33.5	69	2.03
Bubbling (28 mm. tube)	100	26	2.0	38		2.02
Bubbling (18 mm. tube)	117	15.3	1.1	31.1		2.02

[a] A larger charge of oil in meter.

Bubble Size.—The constancy of $L_g/\nu h_0$ can be expected to be maintained only if the character of the foam does not radically change with temperature and the bubble size is constant; since although equation (19) does not contain bubble size explicitly, it is usually a factor in the limiting foam density d_T. The criterion for constancy of $L_g/\nu h_0$ according to equation (19) is constancy of d_T. An illustration of the influence of the limiting relative foam density is provided by an experiment with Oil B where d_T increased to 0.10 on very rapid bubbling at low temperature (as compared to 0.05 in most experiments) because coalescence on the sintered glass bubbler led to larger bubbles. In this case $L_g/\nu h_0$ was 1.0, instead of the mean value 2.0 in Table V.

The effect of bubble size on the average life of the gas in the foam has been investigated by Hoffmann and Peters[3] for their dynamic foams. Analysis of their data reveals that L_g was proportional to the -0.86 power of the bubble diameter.

Another influence of bubble size on foam stability is illustrated when stable bubbles are stretched by gradually reducing the pressure on evacuation; after a certain point they become unstable and rapidly break.

Dynamic Foams.—The dynamic foam methods of Bikerman[2] and Hoffmann and Peters[3] rely on the existence of a dynamic equilibrium between rates of formation of the foam and its rate of collapse at the top. The unit of foaminess, designated Σ by Bikerman and τ by Hoffmann and Peters is given by the equation

$$\Sigma = h/u \tag{20}$$

where h = dynamic height of the foam; u = linear velocity of the gas in the foam.

Hoffmann and Peters observed the same wet foam both by dynamic and static methods, by shutting off the gas supply after the dynamic foam height had been observed and allowing the foam to collapse without further disturbance. Extrapolation of the initial linear rate of collapse to the time axis yielded an intercept numerically equal to Σ or τ. This is the case because at equilibrium the rate of collapse of the foam is equal to the rate of gas flow, u, hence the intercept on the time axis is h/u which is equal to Σ by equation (20). It may be noted that in this case L_g' is $^1/_2\Sigma$. The relation between static and dynamic methods and between Σ and L_g' is shown in Fig. 10. The factor $^1/_2$ arises because in the static measurement the lifetime of the bubbles is taken as starting when the gas is shut off, although they have already been in existence at that instant for an average time of $^1/_2\Sigma$.

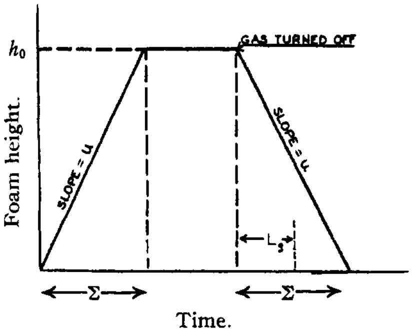

Fig. 10.—Comparison of average life of gas in dynamic and static foams.

In the dynamic method, if the rate of gas input is tripled, for example, the value of h is also tripled, maintaining the same value of Σ and of L_g. However, an application of Equation (19), in the same way as was done in the last column of Table V, gives values of $L_g/\nu h$ which are no longer constant, since $L_g/h = u/2$. Some fundamental difference clearly exists between the foams of Table V, which are uniform and homogeneous, and the wet foams derived from a dynamic bubbler such as used by Bikerman and Hoffmann and Peters. In the former case all the liquid is turned into the foam and the height of the foam is independent of the rate of gas flow, while in the latter case special precautions are taken to ensure that *not* all the liquid is converted into the foam, so that the foam height *is* proportional to the rate of flow. The foams treated in Table V are therefore initially of uniform film thickness while those discussed by Hoffmann and Peters have a gradient of foam density throughout the column at the start of the experiment. This gradient is determined by the rate of gas flow. In equation (18) the foam density gradient, denoted by its function β (see equation 16), while rightly taken as constant for the foams of Table V, cannot be so taken for the non-uniform, inhomogeneous foams discussed by

Hoffmann and Peters. In those latter foams the foam density gradient can be calculated by means of equation (15), since $A/t_2 = u$ and L_g remains constant.

The relation between Σ and L_g has been tested experimentally. Previous attempts to find an experimental relation between dynamic and static methods have failed[8] because comparable units were not employed. The present analysis makes it clear that in the earlier work Σ (dynamic) was compared to L_l (static) with which it does not necessarily bear any correspondence. In Table VI values of L_g (static) are compared with Σ (dynamic), the latter values being obtained from a dynamic foam meter with a capillary bubbler. As pointed out above, the absolute values of the two units cannot be expected to be the same since the foams are not the same, but it can be seen from the last column in the table that the ratio of the foam stability of the lubricating oil to that of the white oil is comparable in the two systems.

TABLE VI

COMPARISON OF RESULTS OBTAINED BY DYNAMIC AND STATIC METHODS

Liquid used	Unit	Value of unit in c. g. s. at 25°	Ratio
White Oil 1	Σ/ν	6.3×10^{-2}	1.1
Oil A		5.8×10^{-2}	
White Oil 1	$L_g/\nu h_0$	1.56×10^{-3}	1.0
Oil A		1.57×10^{-3}	

Summary

1. A foam meter for the measurement of foam stabilities at different temperatures is described, employing bubbling as the method of producing the foam.
2. Foam stabilities of several types of materials are measured and reported.
3. The static foam units L_f, L_l and L_g are shown to be applicable to different types of material and very different methods of foam measurement.
4. An analysis is made of the various factors that operate in influencing values of L_f, L_l and L_g and the resulting mathematical equations tested by the experimental data here reported.
5. The unit L_g can be converted into a function that expresses the static foam stability of a liquid. For foams of the same character, this function is independent of temperature, viscosity, amount of liquid sample taken, method of producing foam and dimensions of the apparatus.
6. The relation between dynamic and static methods of foam measurement is pointed out.

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RECEIVED APRIL 24, 1944

[PAPER NO. 110 OF THE LABORATORY OF SURFACE CHEMISTRY, CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, AND THE UNIVERSAL OIL PRODUCTS COMPANY]

Surfaces of Solids. XI. Determination of the Decrease (π) of Free Surface Energy of a Solid by an Adsorbed Film

BY GEORGE JURA AND WILLIAM D. HARKINS

I. Introduction

The most important effect of the adsorption of a vapor upon a solid is the decrease (π) of free surface energy which accompanies the adsorption. This quantity is, by definition, the film pressure. The value of π is given by the equation

$$\pi = \gamma_S - \gamma_{S_f} = \gamma_0 - \gamma \qquad (1)$$

in which γ_S is the free surface energy of the clean surface of a solid, and γ_{S_f} is the same quantity when the surface is covered by a film. In the more general form of the equation γ_0 represents the free surface energy of any clean surface, and γ that of the surface covered by a film. The free surface energy is the same quantity as the surface tension, which in the case of a liquid may be determined directly, whereas with a solid some other type of experimental method needs to be employed. For this purpose a relationship between the reduction of the free surface energy and some other thermodynamic quantity must be established, and in the case of a solid the simplest of these is the fugacity of a vapor which is adsorbed by the surface of the solid. A method developed on this basis is also applicable to the surface of a liquid, but lacks the simplicity of the direct determination of surface tension.

What is actually involved is the fugacity (f), rather than the pressure, but the two are usually so nearly equal that either may be used. Such equations are applicable to adsorption from solution as well as to that from a vapor phase whenever the fugacity is employed. Examples of the phenomena involved are found (1) in the spreading of (insoluble) stearic acid on water, and (2) in the adsorption of nitrogen on the surface of crystalline TiO_2, and (3) of butyl alcohol from the aqueous phase upon the surface of the water. This paper gives a discussion of the methods used to calculate the lowering of the free surface energy of a solid by an adsorbed film.

II. Theory

Since the change in free surface energy of a solid surface cannot be measured directly, recourse must be taken to some indirect method. Bang-