THE PHYSICAL CHEMISTRY OF FOAMS[1]

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I. Introduction

A parallel exists between the conception of emulsions and the conception of foams. Not only are foams similar to emulsions, but they may be considered, to a certain extent, as concentrated emulsions having a gas instead of a liquid as the dispersed component. On the other hand, the fact that the formation of an emulsion is often accompanied by the formation of foam indicates that at least in these cases the conditions under which foam systems originate are identical with those of emulsions. Oils, readily emulsified in water, act as foam-forming substances, while difficultly emulsifiable oils, such as cedar or castor oil, show very little tendency to form foam. Foams, as well as emulsions, are generally three-component systems, that is, they require the presence of an agent for their formation. Factors influencing the origin of foam systems and those influencing their ability to sustain themselves indicate another similarity between the properties of emulsion and foam systems.

Three stages may be differentiated in the life of dispersion systems such as emulsions and foams: (1) origin; (2) maintenance of the stability of the system formed; and (3) transition to the unstable state.

Factors and forces governing different stages in the existence of a foam comprise the physical chemistry of the system in question.

II. Foam Formation

A. THE ORIGIN AND MECHANISM OF FOAM FORMATION

1. The formation of a single lamina

Foam is a formation in which macroscopic, microscopic and/or ultramicroscopic gas bubbles are separated by micronic or submicronic liquid layers (skins). Therefore, foam is a union of laminae. The formation of a foam occurs in the same manner as the formation of a single liquid lamina. Each film formed serves as a basis for the formation of other surface films, so that knowledge concerned with the formation of a single film may account to some extent for a number of films called in the aggregate "foam." The construction of a foam system may be described as follows. A bubble of air rising in a liquid reaches the surface but does not break through; it rather lifts up a film in the form of a spherical wedge. A second bubble rises to the top, approaches the surface at a certain point, and is placed under the first film. This determines the formation of a second lamina which lifts the first film on one side so that the amount of air enclosed by these two laminae respectively is separated by a portion of the second lamina, as well as by a partition of liquid. In the event the second lamina originates at a distance, the spherical wedge of the first is then completed, the capillary forces and flotation of light bodies assisting the second bubble to approach the first bubble in order to create a tangential contact provided they are not separated by too great a distance, which is not the case in foam formation.

Actually, only a part of a bubble reaches the surface and wets it. The faces of the bubble change in curvature before they touch tangentially, and the same change occurs also along the line on which a bubble is bound to other bubbles. Obviously, because of their liquid nature, the two laminae cannot meet each other either at their angles or at their linear edges; for continuity, it is necessary that they be formed along the line of meeting in a small area of concave surfaces placed perpendicularly to this line. But this area is too small to be distinguished, as are the partitions, which unite to form a small mass having its own curvature independent of the respective curvatures of the two laminae and dependent on the difference in the pressure exerted upon the sides of the two volumes of air enclosed. If these two volumes of air are equal, the two laminae belong to equal spheres, compressing the two volumes of air with the same intensity. But if the volumes of air are unequal, the two laminae belong to spheres of different diameters, exerting an unequal pressure on the two volumes of air. Consequently the partition, when subjected to equal pressure on both sides, is not curved, but plane, and when subjected to unequal pressure, is distorted on one side, the partition diminishing until the pressure produced by it in the concave curvature counterbalances the elasticity of the air.

Since air bubbles are always rising, the structure formed is lifted continuously. All laminae are layered with more or less symmetry, depending upon the difference in the volume of air bubbles and the distribution of points where they may reach the surface of the liquid, the air bubble structure growing higher and higher.

Observation reveals that this accumulation of bubbles is not governed by chance, but is subject to law, that is, innumerable bubbles join together in threes at equal angles in such a way that not more than four edges of three laminae pass through the same point, cutting laminae, as well as edges, at an angle of 120°. Therefore, foam bubbles, in cross section, are hexagonal structures with equal angles of 120° (44).

In figure 1 a configuration of a group of four bubbles, assumed to be equal in diameter and combined rectangularly, is graphically presented. But since this structure is in a state of temporary equilibrium, a transition from this structure to a structure in which three laminae are joined together at an angle of 120° may occur. In this same figure there is also included a projection of assembled curved laminae connected with one another by other laminae extending the length of the prism.

In the formation of a foam, bubbles are formed in which more than three laminae come together, the laminae sliding over one another until conditions for true equilibrium are fulfilled. The motion of the liquid, when displaced by a bubble, lifts up the skin formed and is such that it stretches the two surfaces where the liquid comes in contact with the air. The liquid film or lamina may be stretched only when surface tension and vapor pressure are small. In 1869, Mensbrugghe (37) proposed a formula for the equilibrium of a lamina resting on the same liquid from which it originated (refer to figure 2 for graphic presentation).

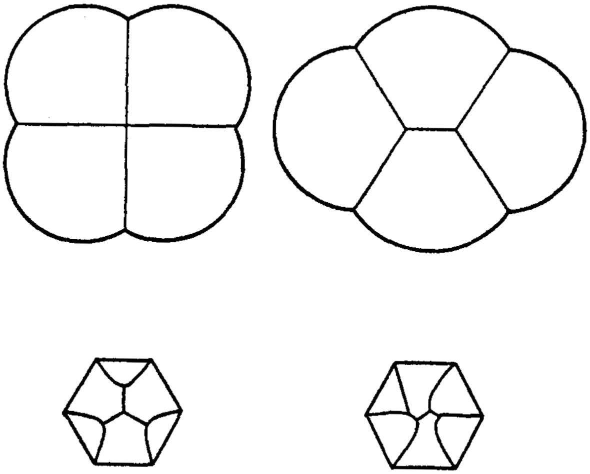

FIG. 1. A GROUP OF FOUR BUBBLES AND A PROJECTION OF ASSEMBLED CURVED LAMINAE

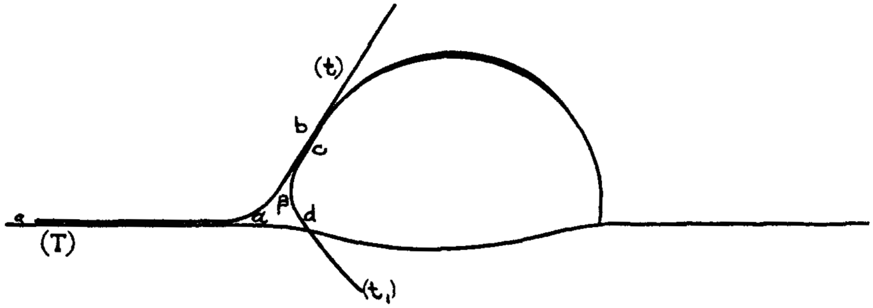

FIG. 2. GRAPHIC PRESENTATION OF A LAMINA RESTING ON THE LIQUID FROM WHICH IT ORIGINATED

In figure 2 the interior surface of a bubble is concave.

2. Forces acting in a lamina

The surface tension, T, of the external liquid at a, the horizontal components of two surface tensions t at b and c, and the horizontal component of a single surface tension t' at d are the forces which tend to displace the liquid contained in the area bounded by curves ab and cd and line ad (figure 2). (These tensions are all directed against the exterior of the small mass of the liquid.) If α and β represent angles formed by tangents with the horizontal in b or c and in d, then we have:

$$T = 2t \cos \alpha + t' \cos \beta$$

According to Mensbrugghe if, in the case of an aqueous soap lamina formed on the surface of the same liquid from which it originated, tensions T, t, and t' are equal to each other, the equation is then written:

$$2\cos \alpha + \cos \beta = 1$$

Or, if the lamina is very large, the pressure produced upon the air enclosed is very low; therefore, β is close to zero, α close to 90°, and the lamina hemispherical.

If the dimensions of the sphere decrease, the pressure of the air on the interior, as well as β, increases with a gradual decrease in α; the lamina would then constitute a portion progressively smaller than a complete sphere. Also, it is evident that if $\cos \alpha$ is close to 1, then $\cos \beta$ is close to -1. This is in the case of an extremely small air bubble; in the surface of the liquid, practically no bubbles originate.

3. Construction of a foam system

In passing from a single liquid lamina to a system made up of a number of laminae, it is of great importance to consider the surface tension factor. Quincke (46) and Marangoni (35) studied the conditions under which a liquid spreads into a thin film, concluding that: (1) Surface tension exists in all liquid surfaces and therefore in all films and is independent of the curvature of the surface or film. This surface tension is the same for all directions of the surface or film and at every point. (2) Surface tension varies with the nature of the liquid. (3) For the same liquid, surface tension varies inversely with the temperature, but at ordinary temperature undergoes little change.

Many hypotheses have been proposed to account for surface tension: according to Segner (56) surface tension originates from the mutual attraction of molecules in the superficial layer tangential to the curvature of this layer; according to Mossotti (41), Hough (26), and Dupré (12), surface tension depends upon the asymmetry of molecular action in the thickness of the superficial layer, although only minor differences in this type of asymmetry are involved; Hagen's (17) hypothesis attributes surface tension to a great density of the superficial layer; the hypotheses of Lamarle (29) and Henry (23) consider surface tension to be due to the contraction of the superficial layers, one portion of the molecules in this layer passing into the interior, thereby decreasing spreading.

According to the work of Laplace, who considered only the effect of curvature, the pressure from a concave layer in a state of equilibrium opposes a force originating in general hydrostatic actions. It must be borne in mind that convex and concave superficial layers exert a normal pressure on a liquid at each point, the superficial layer, meeting an opposing force, finally spreading after curving beyond a critical point. In other words, molecules in the same layer must be in a condition to spread tangentially; this is the reverse of Young's theory, which assumes surface tension and shows that the tangential component of the surface tension around a given point has a normal pressure as a resultant independent of whether the surface is convex or concave. This pressure, as Laplace showed, exists only because of molecular attraction and may be analyzed around a point into tangential components, each of which constitutes a surface tension.

Plateau states that surface tension is a result of curvature, but is independent of the value of this curvature. From an actual consideration of the two tangential components of a convex surface of a liquid and the initial pressure which causes their appearance, it is evident that if the curvature decreases this pressure decreases at the same time but, on the other hand, the angle between the two components increases in such a manner that these components or surface tensions retain the same value as for the previous curvature. If the curvature decreases up to a point where it disappears, the component effected by pressure is eliminated and the two remaining components become prolongations of each other; therefore curvature is infinite, as in the case of plane liquid surfaces.

Another question to be considered is how surface tension penetrates similar surfaces, for instance, a film of liquid adhering by its edges to the surface of a liquid, or to other films. In the case of films, these partitions are invisible, but their existence is obvious. As previously stated, the faces of the bubbles change their curvature before they touch tangentially.

4. Conclusions

1. Foam is a union of laminae.
2. The mechanics of foam formation is similar to that of a single lamina.
3. The symmetry in the construction of a foam depends upon the difference in the volume of gas enclosed by a lamina.
4. The accumulation of bubbles in a foam follows Plateau's rule, that is, bubbles join in three at angles of 120°.

5. Physical factors involved in the spreading of a liquid into a thin film apply to foams, surface tension being one of them. Surface tension is the result of curvature and independent of the value of curvature. Surface tension is the same at every point in all tangential directions. Surface tension varies with the nature of the liquid and inversely with temperature. The change in curvature of the faces of bubbles prior to their tangential contact is proof that surface tension penetrates a film.

B. FACTORS INFLUENCING FOAM FORMATION

1. Vapor pressure and surface tension

Not every gas bubble distribution in a liquid, as in a sol, can be designated a foam. Foam formation combined with a great increase in surface is possible only when the surface tension of the foam components is small.

Pure liquids with low surface tension are close to their boiling points and have a high vapor pressure. Therefore, thin liquid laminae of which foam is composed evaporate too quickly to form and sustain foam. On the other hand, when liquids have a low vapor pressure, their surface tension is too great. Low surface tension and vapor pressure when present together in capillary-active substances serve as favorable conditions for the promotion of the foaming process (15). Capillary-active substances, when dissolved in a system, lower the surface tension and are adsorbed in the interface.

That a certain relation between foaming and surface tension of the liquid from which foam originates should be anticipated follows from the fact that solutions containing dissolved capillary-inactive substances not influencing surface tension do not produce foam. Foams do readily occur, however, with solutions of surface-active substances, such as organic salts and acids, sugars, glycerins, alcohols, and esters. Of course, surface-active substances are foam agents only under definite conditions. In certain cases, discussed later, other factors such as concentration, solubility, viscosity, et al., may overcome the influence of capillary activity. Bartsch (3) proved experimentally (figure 3) that foam formation and lowering of surface tension are antagonistic when a certain concentration is exceeded.

Foam formation–concentration curves drawn by Bartsch for butyric, nonylic, and caproic acids and for octyl, heptyl, and amyl alcohols indicate that these capillary-active foam-forming substances lose their foaming ability when a certain saturation is exceeded. The upper curve b/c of butyric acid has a shape indicating that the relationship between foaming ability and surface tension is lost in higher concentrations. The same experimenter also found that even in the case of such strong capillary-active substances as sodium cholate or saponin the foam-producing ability may be lost when supersaturation occurs. Wo. Ostwald and A. Steiner (43) proved with humus sols that a relation does not always exist between surface tension and foam-forming ability. Bartsch pointed out that oleic acid emulsions which do not foam show a pronounced foaming ability in certain concentration intervals, while the latter, as a rule, have a surface tension of an order of magnitude corresponding to water. By comparing the foam-forming ability of various surface-active foam-forming substances, such as homologous alcohols and fatty acids, the relationship between surface activity and foam formation was found to be complex. A parallel was observed when concentrations were studied corresponding to the limited value for foam formation (3) (figures 4 and 5, from reference 3).

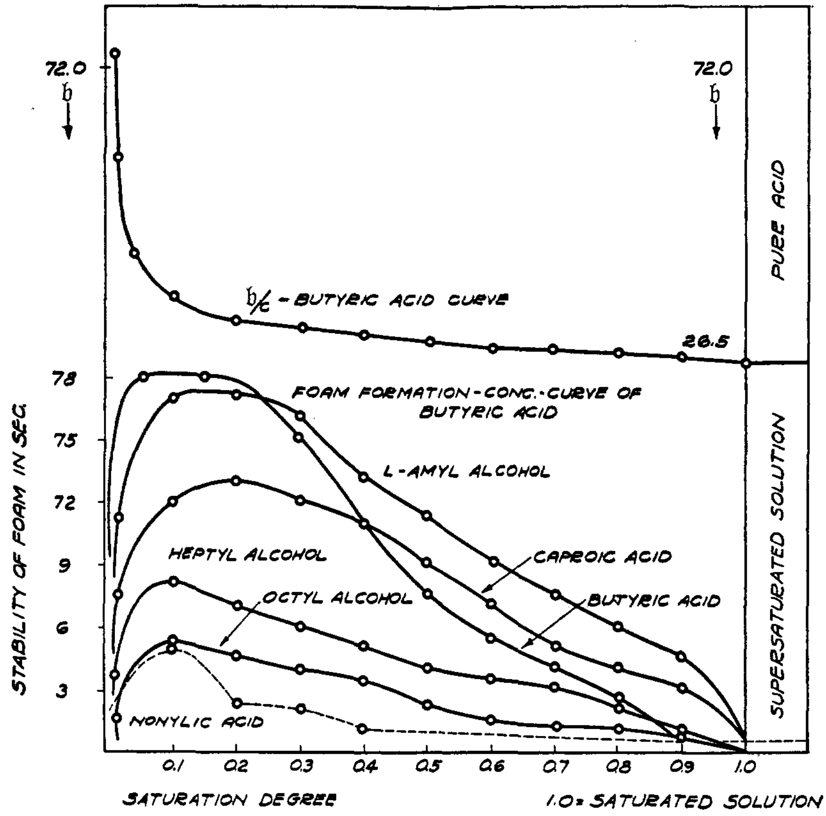

Fig. 3. Surface Tension and Foam Formation

When the maximum in foam formation was reached, the acids decreased the foaming ability in spite of an increase in surface activity, using members

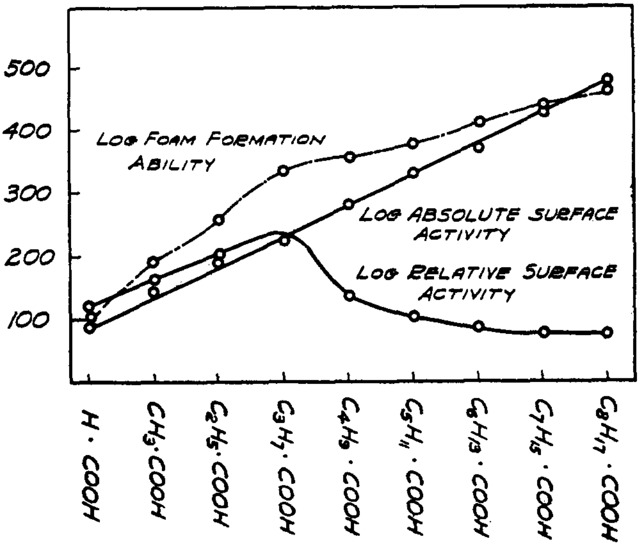

FIG. 4. SURFACE ACTIVITY AND FOAM FORMATION FOR MORE DILUTE SOLUTIONS

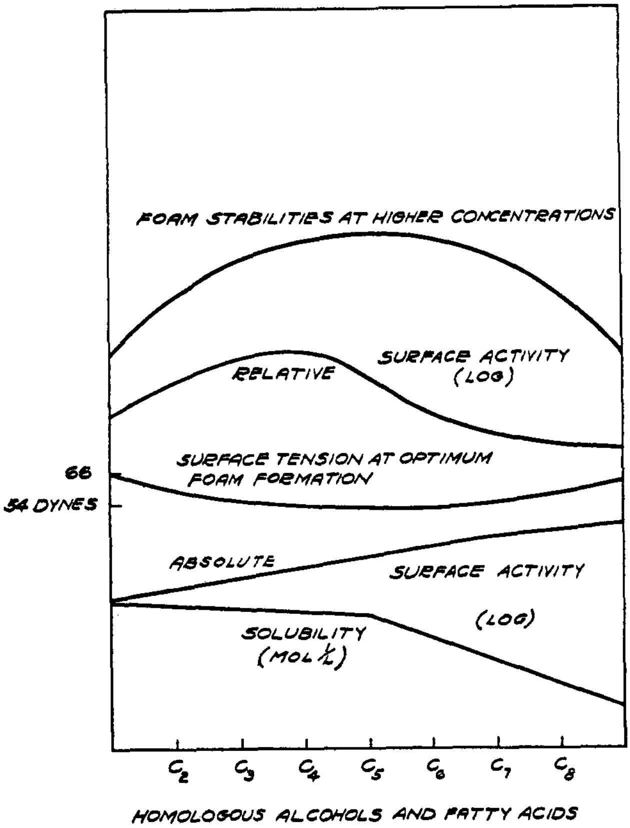

FIG. 5. SCHEME OF THE RELATIONSHIP BETWEEN FOAM FORMATION AND SURFACE ACTIVITY FOR SOLUTIONS OF HIGHER CONCENTRATION

of the homologous series with limited solubility. The only regularity observed by Bartsch was in the group arrangement of surface tension values. The average corresponded to an optimum foam formation at 61 dynes for fatty acids and alcohols. In other cases, the decrease in foaming ability was parallel with the decrease in surface activity of the component dissolved in water. A certain relationship between surface activity and foam formation suggested itself when the solubility of single members of the homologous series was considered. Figure 5, taken from Bartsch's work, shows that foaming ability in very dilute fatty acid and alcohol solutions increases steadily with increasing surface activity.

2. Solubility and surface activity

When surface-active foam-forming substances are dissolved partially or completely in molecular dispersion, solubility of the molecularly dispersed substance also plays a certain part in producing foam. Traube and Klein (67) state that only the molecularly dispersed portion of the solute is related to surface activity, therefore the solubility factor must also be considered in foaming. Solubility decreases with increase in the number of carbon atoms; thus the higher members of the series have a limited solubility or are insoluble. On the other hand, Traube's rule indicates that capillary activity increases in ascending the homologous series. The decrease in solubility limits, therefore, the increase in surface activity. This fact led Bartsch to assume that the maximum solubility is reached by the lowest members of the homologous series and the maximum capillary activity by the highest members. Therefore, a favorable relationship should exist between solubility, surface activity, and foaming ability for the respective intermediate members, such as butyric acid or amyl alcohol. In the case of higher members, this relationship appears to be more unfavorable because the solubility decreases more readily than the surface activity increases.

This assumption may be proved by taking into consideration the well-known equation of Szyszkowski, who formulated an empirical expression of the relationship between σ (surface tension) and concentration (c)

$$\Delta = \frac{\sigma_M - \sigma_L}{\sigma_M} = b \ln \left(\frac{c}{k} + 1 \right)$$

where σ_L denotes the surface tension of the solution, σ_M denotes the surface tension of the solvent, and k is a constant.

By means of Szyszkowski's (61) formula, values for surface activity relating to solubility are obtained when the constant k, the reciprocal value of which is a measure for capillary activity, is divided by the amount of surface-active substance in a given volume of solution. The greater the surface activity and the solubility, the smaller the value of the quotient.

The influence of solubility is also quite considerable; thus an increase in the solubility of a substance forming the foam leads to an increase in foaming (3).

In case a second agent is added to a solution of a capillary-active substance, the foaming ability of the mixture may be improved depending on the changes occurring in the solubility. If the solubility of the first surface-active substance is increased by the addition of the second, then the foaming ability of the mixture may be greater than that of either of the components. For example, nonylic acid, a weak foam agent, becomes an excellent foam agent in a 60 per cent aqueous ethyl alcohol solution. Other foam agents may bring about a decrease in foam formation. In the following examples it was shown that a decrease in solubility brought about by a second capillary-active substance produced a decrease in foaming. A solution of 0.5 per cent of isoamyl alcohol and 0.1 per cent of benzyl alcohol decreased the duration of the foam from 17 seconds to 9 seconds; a *m*-cresol solution and 0.01 per cent of benzyl alcohol decreased the duration of the foam from 11 seconds to 6 seconds. A maximum foaming was obtained with 29 per cent ethyl alcohol; larger amounts caused a diminution in foaming.

3. *Solubility, spreading, and viscosity*

There is another proof for the relationship existing between capillary activity, solubility, and foam formation. Since the solubility of a substance depends on the difference between the attraction of the solute for the solvent and the solute for the solute, it is probable that the work of adhesion minus the work of cohesion, called "spreading coefficient," should also be considered an important factor in determining solubility. But there is a distinction between "spreading in water" and "solubility." In the case of spreading, it is the most active or polar part which is chiefly involved, while the whole molecule relates to solubility. From this standpoint, it is to be inferred that liquids incapable of spreading upon water are insoluble in water. Therefore, the spreading–solubility relationship should be considered in choosing foam agents.

The classical theories (44) ascribe the property of film formation and therefore the property of foam formation to two general factors: (1) viscosity, and (2) low surface tension of the liquid from which foam originates. Since many liquids possessing high viscosity and low surface tension do not form sustained films or foams, many mobile aqueous solutions with a surface tension nearly equal to that of pure water are capable of foaming (36). This assumption has proved unsatisfactory. Tickell (65) observed that gas bubbles liberated from oil upon release of pressure formed a foam. An impure substance containing capillary-active and emulsifying constituents having low surface tension and high viscosity fulfills the requirements for foam formation, according to this investigator. Tickell assumed that low surface tension is necessary for the development of a broad foam surface. Since the capillary-active constituents of an impure complex substance, such as petroleum, may concentrate in the surface films, this condition is satisfied with oils.

The question concerning the distribution of a substance between a solvent and its surface layer has been discussed by Thomson (64) and Ramsden (48). Zawidski (73) measured aqueous acid solutions to which a sufficient amount of saponin had been added to insure a stable foam on shaking. He proved that the composition of the solution differed from its surface layer, the concentration of the saponin in the surface layer being greater than that in the interior of the solution. This fact agrees with the viscosity and tension relation of aqueous saponin bubbles investigated by Plateau. Under similar experimental conditions, the ratio of concentration of saponin in the foam to that in the solution is not constant. When air is led through an aqueous saponin solution and the foam formed is removed after a certain interval of time, the solution ceases to produce foam, while the foaming ability is definitely increased in a condensed foam; therefore, it is apparent that all the saponin is carried away by the foam. Zawidski ascertained this phenomenon by refractometric measurements. He also observed a second phenomenon, namely, that when alcohol is added gradually to an aqueous solution of saponin a certain point is reached at which the ability to form foam on shaking is eliminated. Zawidski explained this phenomenon by stating that alcohol diminishes the surface tension of water much more than that of saponin. This phenomenon of eliminating the ability to form foam was also observed when solutions of isobutyric acid were added to water, thus greatly diminishing its surface tension. Even a large addition of saponin did not produce a stable foam in this case, but a stable foam was obtained by neutralizing the acid with a base.

On the other hand, it was found that if a capillary-active substance was added to a certain foaming liquid like soap, its ability to foam was maintained if the capillary-active substance had the property of forming surface films or skins.

4. Boundary heterogeneity

Shorter (59) ascribed the foaming ability of a liquid to the existence of a surface pellicle which was considered as being formed from the dissolved substance. This most fruitful idea of the heterogeneity of the surface layers of a solution was treated theoretically by Gibbs. He proved from thermodynamical considerations that if the addition of a solute lowered the surface tension of the solvent, the solute existed in a higher degree of concentration in the surface layers than in the solution. The decrease in the surface tension is nothing more than positive adsorption and the excess concentration in the surface towards the solution:

$$x = -\frac{c}{RT}\frac{d\sigma}{dc}$$

where c denotes the concentration of the solution, R and T are constants, and $d\sigma$ is the surface tension decrease.

This deduction of Gibbs was verified by a number of investigators. Lewis (34) measured the surface excess of various solutes in the case of the interface between various solutions and hydrocarbon oils and found in nearly all cases that the measured excess was very much larger than the theoretical value. Thus in the case of a solution of sodium glycocholate the measured surface excess was found to be 5.4×10^{-6} g. per square centimeter, while the theoretical value was 7.0×10^{-8} g. per square centimeter. Shorter explained this discrepancy as follows: Gibbs' theory is applicable to cases in which the process of formation of the surface layer is a simple reversible effect, while Shorter's experiments on surface layers formed by solutions of saponin, peptones, and albumin showed that the process is thermodynamically irreversible and therefore outside of the scope of Gibbs' theory. Bartsch's investigations showed that the maximum of foam-forming surface-active substances depends considerably on the abrupt drop in the concentration, and that this does not apply to skin-forming substances. Surface tension–concentration curves of aqueous solutions for surface-active substances revealed that the foam-forming concentration coincides with the interval of the steep part of the curve and, conversely, the steep part of the curve indicates that a concentration excess in the Gibbs layer is relatively large for these concentration intervals. This maximum for foaming ability is reached for aqueous surface-active substances when the concentration difference in the boundary layer possesses a maximum value. In case of skin-forming substances the concentration excess in the Gibbs layer, as a result of gel formation, is considerable and the concentration drop between the layer and the solution is very steep.

Regarding the structure of the Gibbs layer at the maximum of foam formation, two cases deserve consideration: (1) When concentration is infinitely small, the Gibbs layer is composed of water molecules. (2) When concentration is infinitely large, i.e., saturated, the Gibbs layer consists of molecules of surface-active substances.

These two extremes, in which the boundary layer is homogeneous with reference to the types of molecules, do not induce foaming. In all intermediate cases, in which this layer is made up of two types of molecules and is therefore heterogeneous, foaming occurs. The foaming ability of very dilute or very concentrated solutions having homogeneous boundary layers is small because in the first, water molecules, and in the second, surface-active molecules, predominate. Thus the foaming ability increases when the boundary layer becomes heterogeneous (3). From this standpoint, the addition of a second surface-active substance makes the foam less stable. When this addition causes an increase in surface-active molecules in the boundary layer due to the presence of water molecules, the second substance increases the homogeneity in relation to the molecules of the surface-active substance already present and as a result of which the foaming ability decreases.

The decrease in foaming in the case of high molecular members of the homologous series with an increasing tendency for colloidal solubility is explained by its action contrary to heterogeneity due to the formation of large homogeneous molecular aggregates. The molecularly dispersed members of the series have a greater heterogeneity of the Gibbs layer than the corresponding members partially colloidally dissolved. From this viewpoint, solutions of surface-active substances foam better the more abrupt the concentration drop between the Gibbs layer and the solution, as mentioned previously, and the more heterogeneous the Gibbs layer involved (59). High surface activity, low molecular solubility, and homogeneous boundary layers favor abruptness in the concentration drop (3). Only in intermediate members of the homologous series do both conditions exist.

With respect to colloidally soluble organic liquids, like oleic acid, turpentine, etc., it is assumed that only those capable of spreading on a water surface act as foam formers. The velocity of spreading is not parallel to the rate in surface increase in the formation of homogeneous layers, therefore there is no possibility for the formation of homogeneous layers, and the foam walls consist of heterogeneous boundary layers (molecules of water and organic substances).

Iliin (27), discussing adsorption and superficial energy at the boundary of various phases, points out that a substance dissolved in water is called active when a slight change in its concentration (c) greatly changes the surface tension at the air–solution boundary and that the measure of the activity of the dissolved substance taken in the sense of surface tension (surface activity) is expressed by the equation:

$$g = \frac{\partial \sigma}{\partial c}$$

Neither the activity of an adsorbent, nor the activity of a dissolved substance is involved in Iliin's conception, but only the mutual phase activity of two or more phases at their boundary. As activity, the gradient of certain energy effects, depending upon the change of one of the variables, especially concentration, is envisioned. Consequently, a gas which has a relatively small adsorption heat and adsorption activity at the same time shows great change in σ,—a great surface activity as a result of the difference between surface tension of the gas and the adsorbent. Ramsden (50) indicates that adsorbed molecules in a foam are held in direct contact with both gas and water. There is evidence that before adsorption becomes too great every molecule of the foam agent entering into the surface region is forced to the actual interface and, although still soluble, is retained there permanently.

Shorter (58), in his article "On a Classification of Foaming Solutions," states that in order for solutions to be able to form foams they should have a surface tension capable of local variations. This power of local variations in surface tension is due to the existence of a pellicle called the Gibbs layer. Differences in the foaming nature of various solutions considered important by Shorter are not the same as those pointed out earlier by Plateau. Shorter's classification of foam solutions is based upon two distinct points to be considered with respect to the foaming phenomenon: (1) the nature of the process of the formation of the surface layer, and (2) the manner in which the surface layer contributes to the stability of the liquid film.

The process of the formation of the surface layer varies in different solutions. In the case of a mixture of acetic acid and water, equilibrium between surface layers and the solution itself is obtained readily, except in very dilute solutions, so that the process of the formation of the surface layer may be thermodynamically reversible (10). In soap and saponin solutions, the process assumes another nature. Millner (40) observed in solutions of sodium oleate an irreversibility of the formation of the surface layer. In dealing with solutions of saponin, peptone, and albumin, Shorter (57) showed that the formation of a surface layer proceeds for several weeks without indication of an equilibrium. The substance forming the surface layer separates from the body of the solution at a rate independent of the thickness of the surface layer and continues to separate for some time without any sign of equilibrium. This process is thermodynamically irreversible, but in albumin solutions, it appears to be "chemically" irreversible, the film substance being insoluble in water (49).

Shorter classifies foaming solutions into three distinct classes having the following characteristics: (1) Surface concentration thermodynamically reversible; superficial viscosity or rigidity absent. (2) Surface concentration thermodynamically irreversible; superficial viscosity or rigidity absent. (3) Surface concentration thermodynamically irreversible; surface layers especially viscous or rigid.

In case the foam-producing agent is a solid body, the spreading and wetting factors are of significance. Substances less wetted by water adsorb capillary-active substances from aqueous solutions more readily when building the Gibbs layer. Hydrophobic galena, copper pyrites, and zinc blende are not readily wetted, and therefore pass into foam. Quartz and feldspar are hydrophilic and, consequently, are well wetted; therefore they remain in the water when separated from their ores in the flotation process.

Substances like sulfides, insoluble oxides, carbonates, carbon, insoluble sulfates, and metals, in fact all substances, as shown by Reinders (53), which attach themselves to the boundary by distribution between two liquids, or are completely surrounded by a liquid, may be used as foam agents. Reinders and Hoffman (54) investigated adsorption through adhesion at the liquid–gas interface; the theory of these processes was developed by De Coudres (9). When two liquids come in contact with a solid body, then one of these liquids may displace the other and surround it completely; alternately, each liquid may surround the solid partially with the formation of an edge angle at the contact surface.

In the first case we have a complete wetting by one of the two liquids, while in the second case only a partial wetting takes place, the latter occurring when an aqueous suspension of a solid substance is mixed with a second liquid insoluble in water as in the case of water–oil emulsions. When liquid–gas systems, instead of liquids insoluble in water, are dealt with, the gas phase is present. When water displaces the gas phase from the surface of the solid particles, the latter are completely wetted by water and no precipitation occurs. When only a partial displacement of the gas phase occurs with the formation of an edge angle, then the solid particles are attracted to the liquid–gas interface and the aqueous surface layer floats freely. Valentiner (69) actually showed that a powder may float better the larger its edge angle.

Relationships become more complicated when a molecularly or a colloidally dispersed solution comes in contact with gas in the presence of a surface of solid particles, such as a foam-producing agent or a stabilizer.

Surface tensions at phase boundaries lose their characteristic fixed values, which cause homogeneous wetting ability, and become functions of the concentration of the dissolved substance. The relation between adsorption and wetting ability was also investigated by Traube and Kicke (66), who found that substances which are not readily wetted by water adsorb caprylic acid from aqueous solutions more readily than substances which are more readily wetted by water. The solid phase may also lose its foam-forming ability when a substance insoluble in water and which wets the solid phase more readily than does water itself (chloroform, for example) is added. Further investigations of Traube and Nishizawa (68) on the adsorption of caprylic acid on minerals showed a relation existing between wetting ability, adsorption, and flotation.

The process of separating particles of finely ground ore from the particles of gangue by flotation is an application of surface phenomena. This process is based on the fact that mineral sulfides, e.g., galena, are wetted by certain oily liquids, but not by water, whereas particles of quartz are wetted by water and not by other liquids. Therefore, if the finely divided ore is agitated with an oil–water froth, the sulfide particles are preferably wetted by the oil films surrounding the bubbles of the froth, while the quartz remains in the water phase. The sulfide particles which attach themselves to the bubbles are floated to the surface by a stream of air and separated from the gangue particles which remain at the bottom of the container. Harkins and Feldman (14) state that since the free surface energy of almost all inorganic solids is high, their work of cohesion is of the same order, and the work of adhesion is also high with reference to practically all liquid substances. Since the work of cohesion in water and organic liquids is generally low, the values of the coefficient of spreading of these liquids upon such solids should generally be high. Therefore the spreading of these liquids should occur upon such solids when their surfaces are pure.

Among other factors, the spreading ability of liquids forming foams indirectly plays an essential part in determining foam formation. Briefly, these views of the criterion of spreading of one liquid upon the other are as follows:

1. According to Lord Rayleigh (52), all liquids spread on pure water.
2. Liquid b spreads on liquid a if T_a is greater than $T_b - T_{ab}$, where T_{ab} represents the interfacial tension between two liquids and T_a and T_b the respective surface tensions. Non-spreading conditions exist when T_a is less than $T_c - T_{ab}$.
3. According to Langmuir, liquids whose molecules are polar or contain polar groups spread on water.
4. According to Harkins, a liquid spreads if its work of surface cohesion W_c is less, and will not spread if its work of surface cohesion W_c is greater than its work of adhesion W_a with respect to the liquid upon which the spreading is to occur.

Harkins (19) developed a spreading coefficient by thermodynamic reasoning, using two hypotheses as a basis. Only large scale motion is of importance in spreading and only free surface energies are involved. The free energy decrease is $S = \gamma_a - (\gamma_b + \gamma_{ab})$, where γ_{ab} represents the free energy of the interface. The work of adhesion W_a is given by the equation of Dupré as $W_a = \gamma_d + \gamma_b = \gamma_{ab}$. The work of cohesion is $W_c = 2\,\gamma_b$. A combination of three equations $S = W_a - W_c$, indicates that spreading occurs if the adhesion between two liquids is greater than the cohesion in the spreading liquid. Thus positive values of S correspond to spreading and negative values to non-spreading. In general, Harkins assumes that the value of the coefficient increases as the electromagnetic field around the molecules becomes more asymmetrical. This is due to the fact that in the case of asymmetrical molecules the work of adhesion towards water is greater as compared with the work of adhesion when symmetrical molecules are involved. This excess work of adhesion of asymmetrical molecules towards water may find its explanation in the rupture of very strong electromagnetic fields, while in the case of separating water molecules from water only the weakest fields are ruptured. It is evident from the above that spreading of liquids in the process of foam formation becomes an important factor, especially when solid agents participate in the production of a foam system where forces of adhesion and cohesion come into play.

5. Conclusions

1. Capillary-active substances promote foaming at a definite concentration.
2. An abrupt drop between the concentration of the boundary layer and the solute is a requisite for foaming.
3. The relation between the solubility and the surface activity of a foamer determines whether it is strong or weak.
4. Foaming, as a rule, occurs only in the case of a heterogeneous Gibbs layer.
5. Colloidal solubility does not favor foaming. The formation of large molecular aggregates interferes with the principle of heterogeneity.
6. The Gibbs layer in foam systems may differ with respect to the establishment of a state of equilibrium. A distinction is made between thermodynamic and chemical irreversibilities.
7. The wetting and spreading factors are especially emphasized in case the foamer is a solid. Substances less wetted by water adsorb capillary-active substances from aqueous solutions to a greater degree.

III. The Stability of Foam Systems

Although foam systems are closely related in their properties to emulsions, yet in their stability they differ greatly. The life of foams is short in comparison with the life of emulsions. Foams are rather labile formations because in other dispersion systems a true static equilibrium is possible,—the kinetic energy of molecules creates a considerable opposing action. This kinetic resistance is absent in foam systems.

On the other hand, combined with a much greater surface increase, foam formation greatly opposes the tendency of the system to reach a stable state

TABLE 1

Stability of foams according to observations of Plateau

SUBSTANCE	STABILITY	EXPERIMENTAL CONDITIONS
Class I:		
Distilled water	1– 7 seconds	Atmosphere saturated with vapor
	1– 12 seconds	Atmosphere dried with sulfuric acid
Glycerol	– 2 seconds	
Sulfuric acid	1– 28 seconds	Atmosphere dry
Nitric acid	– 1 second	Atmosphere saturated with vapor
Ammonium hydroxide		Atmosphere saturated with vapor
Saturated solution of tartaric acid	1–142 seconds	
Potassium nitrate	– 6 seconds	Atmosphere saturated with water vapor
Sodium carbonate	– 26 seconds	Atmosphere saturated with water vapor
	1– 30 seconds	Atmosphere dried with calcium chloride
Class II:		
Olive oil	0– 7 seconds	
Lactic acid	1– 18 seconds	
Acetic acid	0– 8 seconds	Atmosphere saturated with vapor
Turpentine	1– 6 seconds	
Benzene	Maximum –12 seconds	
Class III:		
Marseille soap	30 seconds–2 hours	
Domestic soap	5– 14 seconds; colorless phase of water vapor; stable about 90 minutes	Atmosphere saturated
Potassium colophane solution	10– 30 minutes	
Saponin solution	25– 40 minutes; colorless phase; maximum stability, 12 hours	
Albumin solution	Many hours; colorless phase; stability may be several days	
Ferric acetate	15– 30 seconds; colorless phase; maximum stability, about 24 hours	

TABLE 2

Maximum foam duration for various substances

AQUEOUS SOLUTIONS OF	OPTIMUM CONCENTRATION	MAXIMUM FOAM DURATION
	moles per liter	*seconds*
Propionic acid	0.26	11.0
Lactic acid	1.00	7.5
Propyl alcohol	0.34	11.0
Glycol	6.00	1.5
Glycerol	6.00	3.0
Cane sugar	0.50	0.5
Ethyl alcohol	0.28	5.0
Propyl alcohol	0.34	11.0
Isobutyl alcohol	0.09	12.0
Isoamyl alcohol	0.036	17.0
tertiary-Amyl alcohol	0.034	10.0
Heptyl alcohol	0.0007	8.0
Octyl alcohol	0.0003	5.0
Formic acid	0.45	4.0
Acetic acid	0.20	8.0
Propionic acid	0.25	11.0
Butyric acid	1.00	18.0
Valeric acid	0.015	9.0
Caproic acid	0.0075	13.0
Heptylic acid	0.0015	16.0
Caprylic acid	0.00025	12.0
Nonylic acid	0.00007	5.0
Ethylamine	0.40	12.0
Aniline	0.10	11.0
p-Toluidine	0.04	6.0
Phenol	0.10	12.0
Benzyl alcohol	0.10	10.0
m-Cresol	0.025	9.0
Nitrobenzene	0.005	6.0
Benzene	—	0.2
Acetaldoxime	0.37	10.0
Paraldehyde	0.03	9.0
Acetone	0.50	2.5
Methyl propyl ketone	0.05	3.0
Ethyl propionate	0.01	2.5

by diminution of the surface with a resultant decrease in surface tension. But this surface tension decrease is subjected to lasting changes in time, and this is the cause of having a dynamic, not a static, equilibrium.

The work of Plateau contains experimental data with respect to the duration of a foam from various foaming solutions; this is summarized in table 1.

Recently the relation between foam duration and surface activity was studied; the results showed that an increase in foam duration is parallel with an increase in surface activity (3). This was the case with fatty acids up to butyric and with alcohols up to isoamyl. Maximum foam duration for fatty acids and alcohols is presented in tables 2 and 3 (experiments by Bartsch). The surface tension of aqueous solutions compared by Bartsch, using a concentration corresponding to the maximum foaming ability as a criterion, shows great deviations accounted for by isocapillarity of the surface-active substances.

TABLE 3

Maximum foam duration for various substances

AQUEOUS SOLUTIONS OF	MAXIMUM FOAM DURATION	CONCENTRATION AT MAXIMUM FOAM DURATION	SURFACE TENSION OF SOLUTIONS AT MAXIMUM FOAM DURATION
	seconds	*moles per liter*	*dynes*
Ethyl alcohol	5	0.28	66
Propyl alcohol	11	0.32	56
Isobutyl alcohol	12	0.09	56
Isoamyl alcohol	17	0.036	54
tertiary-Amyl alcohol	10	0.034	61
Heptyl alcohol	8	0.0007	68
Octyl alcohol	5	0.0003	64
Formic acid	4	0.45	70
Acetic acid	8	0.20	69
Propionic acid	11	0.25	61
Butyric acid	18	1.0	33
Valeric acid	9	0.015	64
Caproic acid	13	0.0075	57
Heptylic acid	16	0.0015	60
Caprylic acid	12	0.00025	66
Nonylic acid	5	0.00007	70
Benzyl alcohol	10	0.1	59
m-Cresol	9	0.025	62
Aniline	11	0.1	62
p-Toluidine	6	0.04	63

A. FACTORS IN THE STABILIZATION OF FOAM SYSTEMS

With regard to factors influencing the permanency of a foam, although the degree of stability is less, a similarity to emulsions is evident.

The following factors imply the conditions under which an emulsion system becomes stable, namely, low interfacial tension, optimum concentration, viscosity, behavior with electrolytes, action of protective colloids, presence of a foam agent, existence of a Gibbs adsorption layer and its thickness, and lastly orientation of molecules in the foam interface. There is also a certain peculiarity in the behavior of foam systems, as compared with emulsions, which may be attributed to their difference in character. As mentioned above, from a purely thermodynamic standpoint it follows that foams cannot be as stable as emulsions. Electrical forces contributing to the stability of emulsions are not so important in the case of foams where capillary forces apparently play a greater part. The dispersion factor does not act in the same direction in the case of foams as in emulsions.

Foam systems may be differentiated as follows (3):

1. Those originating by shaking water and surface-active organic substances,—two-phase foam systems.
2. Those obtained by shaking emulsions of organic substances, as well as lyophilic foams,—three-phase foam systems.
3. Those systems in which the foam agent is a colloidally dissolved phase and acts as an integral part of the dispersion medium in the foam system so that it can not be distinguished from two-phase foams in which the molecularly dissolved foaming agent is also an integral part of the dispersion medium.
4. Those in which a solid phase is present occurring as an independent component of the system and in macroscopic quantities similar to the gas phase.

To comprehend the measurable stability of foam systems, first those systems must be considered in which the foam agent is present as an electrolyte, molecularly or colloidally dispersed, as a protective colloid, or as a solid foam former. In this regard a certain analogy may be drawn between foams and emulsions. Permanent foams, as well as permanent emulsions, under ordinary conditions of temperature and pressure are obtained by using foam and emulsifying agents. Further, the degree of stability of a foam depends upon the nature of the components participating in the system and whether or not foam originates by shaking solutions of lyophilic or lyophobic substances. While the first foam systems are more stable and less sensitive to added electrolytes (analogous to lyophilic sols), the lyophobic substances render the foams unstable and are very sensitive to electrolytes.

1. The influence of electrolytes

Lyophilic foams have more outstanding properties, such as viscosity and elasticity, and the influence of electrolytes is so small that in most cases it cannot be proved. This phenomenon is explained by Bartsch by the fact that the foam walls of these systems consist not of the sol, but of the coagulated sol or gel of the lyophilic colloid, as shown by Ramsden and others. The dispersion medium is in a rigid or semi-rigid state, which acts opposite to the change in dispersion so that no precipitation of electrolytes may be expected. Such foam systems may be sensitized by means of surface-active substances. Bartsch proved experimentally that foam formed by shaking a 0.001 per cent saponin solution, after the addition of 0.5 per cent of isoamyl alcohol, was found to be sensitive to electrolytes. The behavior of unstable foams with respect to electrolytes is similar to lyophobic sols. The only difference is the time of stability; lyophobic sols are stable when compared to lyophobic foams. The speed of coagulation caused by mechanical changes occurring in foam walls is frequently so high that it exceeds the speed of precipitation of electrolytes. Some of these foams are sufficiently permanent and undergo only coagulation induced by electrolytes. Foam duration is usually expressed in the number of seconds from the moment of interruption of shaking of the foam-forming liquid to the complete disappearance of the foam formed. Bartsch investigated foam systems of amyl alcohol, quinoline, turpentine, and eucalyptus oil. The similarity between lyophobic sols and lyophobic foams is obvious from an investigation of the hydroxyl ion influence upon the stability of foams. The hydroxyl ions were found to produce a considerable increase in the stability of foam systems, and a decrease in the number of foam bubbles, increasing the degree of dispersion of the gas phase. On the other hand, hydroxyl ions had a peptizing effect upon the foam system, but this action was limited by the degree of concentration. Bartsch's investigation proved that the duration of a foam formed from an isoamyl alcohol solution was decreased from 18 to 15 seconds by the addition of the following concentrations of electrolytes:

Electrolytes	*Millimoles per liter*
NaOH	30.0
NaCl	1.0
$Na_2SO_4/2$	0.8
$H_2SO_4/2$	0.04
$BaCl_2$	0.05
$AlCl_3$	0.0005

The stability threshold displacement for various electrolytes is well pronounced.

Potassium carbonate and potassium citrate were found to be excellent peptizers. Although the peptizing action is also a function of concentration, Whitney and Straw (71) found that for the peptization of emulsions the favorable concentration lies between 0.2 and 80 millimoles per liter; foam systems show an optimum action at concentrations of 0.1 to 10 millimoles per liter.

2. The action of protective colloids

Further analogy between lyophobic foams and lyophobic sols is found in their behavior with respect to the action of protective colloids. The influence of protective colloids upon the stability of foam systems has also been discussed and proved experimentally by Bartsch. Lyophobic foam systems may be protected from the precipitating action of electrolytes by protective colloids. The actual concentration of the protective colloid in a foam system is doubtful and differs from the starting solution. On account of the decreasing surface tension, lyophilic colloids gather at the boundary surface of the solution. The presence of these substances in a foam is shown by an increase in its stability. Approximately equal amounts of various protective colloids are necessary to increase foam duration to the same extent. Bartsch found that the smaller the concentration, the more surface-active is the protective colloid. Very strong surface-active substances show an extreme deviation (see table 12 in the paper by Bartsch (3)). The relative protective number for foams with respect to the sequence of the protective action was found to be in complete agreement with that of gold numbers for equal protective colloids. A protective colloid may act on a foam system in a direction opposite to the one mentioned above. Since precipitation in the interface is considered a fundamental condition for the formation of a three-phase foam system, it seems reasonable to assume that those protective colloids which prevent this precipitation make the formation of three-phase foam systems impossible. The protective colloids at certain concentrations displace completely the solid phase from the foam system, and in this case an unstable two-phase foam system is formed instead of the three-phase. The alternative explanation favored by Bartsch is that a stable two-phase system develops when the protective colloid is present in the solution in a high enough concentration, because protective colloids themselves are able to build up a stable two-phase foam system. Flotation practice makes use of this phenomenon when the behavior of various ores against certain protective colloids is determined by measuring the weighed amounts of the corresponding ores which may still be adsorbed by the foam at equal concentrations of the colloid.

3. Viscosity as a factor in the stabilization of foam systems

Bartsch also worked out the idea of increasing the stability of foams by the addition of substances increasing the viscosity. He carried out experiments with isoamyl alcohol solutions to which various amounts of glycol and glycerol were added. The result was that only very high concentrations of about 60 per cent increased the stability markedly. This was explained by the action of the "removal law" of Michaelis and Rona (39), according to which glycerol or glycol was partially removed from the foam walls by the presence of surface-active substances. A soap-saponin solution may serve as an example of the "law of removal." In this case, the soap solution has a smaller surface tension than the saponin solution, and this results in the removal of soap from the interface by saponin. The fact that a saponin solution loses its ability to form a stable foam on the addition of alcohol may be partially explained by the same removal process but, on the other hand, it is essential that saponin be really soluble in alcoholic solutions and not form skins.

Quincke (47) was the first to describe the peculiar phenomenon that ethyl ether, present even in small amounts in the surrounding atmosphere, destroys the foam of a good foaming liquid. Again the capillary-active ether removes the foam agent in the liquid. The skin-forming abnormally adsorbed substances, such as soap, saponin, lyophilic foam agents (albumin and gelatin), the adsorption of which is not influenced by capillary-active substances taken in minute amounts, may increase considerably the stability of isoamyl alcohol foam. An amount of 0.000001 per cent of soap increases the foam stability twofold, while 0.001 per cent of gelatin is required for the same action. This depends on the surface activity of the corresponding substances. Stability also depends to a certain extent on whether the foam contains large or small bubbles, and whether the bubbles are elastic or rigid. Certain substances added to a foam-forming solution not only increase the stability by an increase in viscosity, but render a certain elasticity by softening the interface skins, thereby preventing the coalescence of bubbles in a foam.

Boys (6) reports an experiment in which one drop of a soap solution added to 30 g. of a saponin solution was sufficient to prevent the rigidity of saponin bubbles. On the addition of three drops, the surface skin became movable and elastic, as in the case of pure soap solutions. Glycerol added to a soap solution induces foaming, increases viscosity, and, at the same time, assists in the production of soft and flexible skins. Therefore saponin solutions with glycerol resemble, in their behavior, pure soap solutions. Elastic foams and those with large bubbles appear to be more stable. It is probable that an explanation for the stability of durable foams as, for example, those produced by the sea, by beer, or by aqueous solutions of saponin and soap, must be sought partially in the formation of very viscous or semi-rigid or gel-like membranes at the interface. Wheat gum used in the beer industry, as well as other dextrin-like substances, acts similarly to glycerol, increasing the viscosity and producing softer and more elastic skins. That the various degrees of stability of a foam often depend on the properties of the bubbles forming the foam has been proved.

Whether the bubbles are elastic or rigid depends chiefly on the nature of the films. Soap solutions are distinguished by the formation of very elastic bubbles, which show a smooth flexible surface. Contrary to this, bubbles of saponin solutions are much more rigid; when a bubble collapses, a pleated sac is observed. The difference between the elastic lamina of soap and the rigid type of saponin becomes evident from the rearrangement in colors which takes place with a continuous change in the thickness of the lamina. In saponin foams, the laminae are so rigid that certain color spots are retained unaltered upon a given lamina. In the tendency towards equilibrium, some laminae burst or unite to form new ones. But still the history of the laminae in question may be read from these invariable color spots.

4. The action of finely dispersed solids

While the behavior of gas–liquid and liquid–liquid systems in themselves is evidently different, nevertheless certain analogies are met with. Both emulsion and foam systems may be stabilized, not only with agents which are molecularly or colloidally dissolved, but with finely dispersed solids, first applied by Pickering for emulsion systems. The latter may replace solutions in the interface and build up a boundary layer to increase the stability of these systems. Donnan (11), speaking of the stability of foam, states: "If air is violently churned up with water, only comparatively large bubbles are produced and these quickly rise to the surface and burst. If a very small amount of a substance which concentrates at the air–water interface is added, an almost milk-white air emulsion of small bubbles is produced which rise to the surface and produce a relatively durable froth." According to Lord Rayleigh (51), who discussed this phenomenon, it is clear that diminution of interfacial tension facilitates the subdivision or the dispersal of air. The existence of the surface layer confers a certain amount of stability on the resultant foam, since it will give rise to forces which resist the thinning of a bubble wall. Any sudden increase in the surface will produce a momentary diminution in the concentration or thickness of the interface layer and hence an increase in surface tension, which will persist until the normal thickness or concentration is readjusted by diffusion of molecules from the inside volume,—a process which in very dilute solutions occupies a perceptible time. That this explanation of Lord Rayleigh is correct, says Donnan, may be seen from the fact that very often stronger solutions of the same surface-active substance would not foam at all. In this case the readjustment of the equilibrium thickness or concentration in the gas–liquid interface occurs with such rapidity that practically no rise in surface tension and hence no counteracting force comes into play (24). On the other hand, when higher concentrations are taken, aggregates of gas bubbles and solid particles can no longer be formed by shaking, because the interfaces formed thereby are already occupied by molecules of the surface-active substance.

Dynamic equilibrium (2) established between the speed of formation of the adsorbed layers of the foam-forming agent or stabilizer at the solid–liquid boundary on one side and the speed of such layer formation at the gas–liquid interface on the other side determines to a certain extent the stability of this three-phase foam system in the case of higher concentrations of the foam agent. As has been demonstrated in the experiments of Hoffmann (25) and others, small solid particles may contribute to the stabilization of a froth or foam as in the case of the mineralized frothers or the ore flotation process by the preferential aggregation in the interface between two phases. Bechold, Dede, and Reinders (4) state that solids prevent coalescence of bubbles in foams, as well as in emulsions. Solids prevent coalescence of droplets, thus increasing the stability of a system. The degree of dispersion of the solid was found to be of even greater significance in foam systems than in emulsions. Substances in a very fine degree of dispersion increase the foam stability much more than substances of a coarse grain dispersion. There is an optimum dispersion of the solid phase for the stabilization action between colloidal and coarse distribution (2). For example, when lead glance which has been passed through a 900–2500 mesh sieve is used as a foam agent, it increases foam stability to 60 seconds; when lead glance which has been passed through a 9000–12,000 mesh sieve is used as a foam agent, the life of the foam formed is increased to several hours. Further, the amount of the stabilizer, whether it is a liquid acting as a foam-former or a solid, is decisive for the formation of a stable foam. The magnitude and stability of aggregates of gas bubbles and solid particles are determined by the concentration of the foam agent, and the nature and affinity of the foamer and the solvent for the solid phase.

B. FORCES INVOLVED IN MAINTAINING STABILITY

1. *Electrostatic and capillary forces*

Among the forces involved in maintaining the stability of a foam system are electrostatic and capillary forces. Concerning the nature of forces producing an attraction between solid particles and a gas, it is known that all components of a three-phase foam system are charged with electricity of the same sign, gas bubbles being charged negatively against water, therefore stability depends on the valence and the adsorption ability of the cations. The electric influences are indirect rather than direct and seem to be responsible only as to which boundary phase the particles may enter and the degree to which they may coagulate and change the structure of the foam. The charge of the gas phase may be determined by the indirect method, using the ion precipitation series of colloid chemistry. Cations produce a precipitation in various foam systems, according to their valency, and these systems have been found to be negatively charged. Bartsch determined the charge on a gas bubble in a foam system, but the potential drop at different boundaries in the system has not been proved. It is still undecided whether the electrokinetic potentials or the phase boundary forces are dealt with. Where gases are acting, the balloelectric effect should be considered. The fuzzing effect of Lenard (15, 33) is based upon a similar phenomenon fundamental to balloelectricity. A balloelectric effect occurs when gas bubbles pass through a liquid and then leave the surface. The electrical energy from the double layer reaches the gas phase and gives to it a certain charge. Balloelectricity implies streaming potentials, but in this case the charges at the boundary of the liquid (gas) move readily; therefore, not only a displacement, as in the case of streaming potentials, but rather a destruction of the double layer by the tangentially-acting mechanical forces takes place and the electricity carried by both layers (external and internal) reaches the gas. The gas phase was found to be negative, while electrolytes, acids, and certain active substances (8) produce a change in the charge even for small concentrations. In general, electric influences in foam systems have not as yet been thoroughly investigated.

Taggart (62) studied the changes of the potential under the influence of electrolytes. He permitted a small gas bubble to migrate cataphoretically around the longitudinal axis of a rotating glass cylinder between two electrodes and determined the direction of migration and its speed under various conditions. He found that the gas bubble in pure water was charged negatively. The velocity of air, oxygen, and hydrogen spheres in water was found to be about 4×10^{-4} cm. per second per volt per centimeter. The presence of hydrogen ions decreased the boundary phase potential to zero without a change in the sign of the charge. Tri- and tetravalent cations produced a change in the sign of the charge. A sphere of gas in a solution was found to change the sign of its charge as it diminished in size by being adsorbed into the solution. Surface-active substances decreased the cataphoretic speed according to Traube's rule. In general, the interfacial potential differences are of great importance and play a fundamental part in determining the stability or instability of the colloidal state of matter. In the case of foam interfaces, potential differences are not perhaps of such great importance, but since very little work has been carried out in this direction, our opinions as to the importance of this factor must be held in abeyance.

It has been shown only in the case of an air–water surface that there exists an electrical separation or potential difference in the interface layer and that certain substances can produce pronounced variations or even reversal in sign for this electrical double layer. There may be a possibility for direct measurement of the potential drop between single phases of a foam system using the Haber-Klementschewitch glass electrode. The influence of charge upon attraction between components of a foam system is marked only in case other forces, such as capillary forces, are weak. The fact that gas bubbles adhere to solid particles in spite of electrostatic repulsion of the components indicates that the more powerful capillary forces participate to a great extent in maintaining permanency.

The coalescence of two drops takes place at the boundary partition, where a diminution of surface occurs and where capillary forces originate tending to tear apart these boundary sections and to counteract their coalescence. Capillary forces act against molecular attraction,—a cohesion between molecules when dealing with the same kind of molecules and an adhesion when different ones are involved. These forces existing between molecules of similar and different natures, more than the electrical elementary forces, must be considered in the case of three-phase foam systems.

Talmud and Suchowolskaja (63), in their recent study of elementary foams, pointed out that stability depends rather on the degree of hydration and that the slipping velocity of the water layers in the walls of laminae is a determining factor of stability because substances stabilize before the adsorption layer is obtained.

2. The adsorption layer in the interface of a foam system and its thickness as a factor influencing stability: the Langmuir-Harkins orientation theory

As in the case of emulsion systems, so in three-phase foam systems,—for example, amyl alcohol, solid agent (foamer), oleic acid (stabilizer)—a relationship appears to exist between stability, the presence of an interface layer, and its thickness.

Adsorbed molecules are held in direct contact with both gas and water in a foam system. Some adsorption surfaces are extremely viscous or even rigid (saponin and nearly all proteins), and the adsorbed particles are in mutual contact. Others are freely mobile (quinine and soaps), and the particles are either more widely spaced or so oriented that only cohesion between a liquid comes into play. In many cases where adequately permanent bubble films are obtainable, the interference colors developed as the film becomes thinner are disposed in horizontal bands when the surfaces are mobile, but chaotically disposed when the surfaces are rigid.

It is known that gases or vapors can be condensed or adsorbed by solid and liquid surfaces. The question arises whether the formation of primary unimolecular films ever occurs in such cases. Langmuir (30) measured the adsorption of a number of gases at low temperatures and pressures on defined surfaces of mica and glass and concluded that the maximum quantities adsorbed are always somewhat less than the amounts to be expected in a unimolecular surface layer. Carver (7) found similar results measuring the adsorption of toluene vapor on known glass surfaces.

This view that the maximum adsorption from the gas phase cannot exceed a unimolecular layer has, however, been much criticized. Thus Evans and George (13), on the basis of their own measurements of the adsorption of gases on a known surface of glass wool combined with data obtained by Mulfarth (42), concluded that the adsorption layer may be several molecules thick. Reference may also be made to an article by Wilson (72), who deduced from the results of the adsorption of oxygen and nitrogen at low temperatures that these gases are held in layers several molecules thick.

Another type of surface layer formation is at the surface of liquids where a substance dissolved in a liquid concentrates preferably at the liquid–air or liquid–vapor interface. Gibbs (16), and later Thomson (64), showed that if a dissolved substance (in relatively dilute solution) lowers surface tension, it will concentrate at the surface. That such a phenomenon actually occurs in foam has been demonstrated qualitatively in the experiments of Hall (18), Zawidski (73), and Kendrick and Benson. If various experimental values are considered, then evidence is produced that they are not materially different from those found by Langmuir and Adams for the oriented unimolecular layer of practically insoluble fatty acids resting on the surface of the water. Harkins' theory, regarding monomolecular films produced on water, points out that these films occur only when the spreading coefficient has a relatively high value. Since these high values result only when the spreading substance contains a polar group in its molecule, the presence of such a group is essential to a monomolecular film for spreading on water, but not at all essential for the production of a thicker film. Donnan explained the fact that the thickness values in some cases are greater by the partially or completely vaporized state of the adsorption layers.

Adams and Marcelin (1) made the important discovery that the unimolecular surface films which they investigated may pass rapidly, on increase in temperature, from the state of solid or liquid surface films to the state of vaporized surface films in which the "juxtaposed" molecules become detached from each other and move about with a Brownian or quasimolecular motion. These investigators attributed this behavior to the thermal agitation of the water molecules to which they were attached.

Bartsch first emphasized the fact that the stability of three-phase foam systems, analogous to three-phase emulsion systems, depends upon the dimensions of the adsorbed Gibbs layer of the stabilizer. He calculated the thickness of the adsorbed layer from data obtained for the weight of the solid phase, the specific gravity of the solid phase, and the size of the particle given by the degree of dispersion, and found that the adsorbed layer under stable conditions may run up to five to ten molecules thick with a layer of galena, two molecules with copper pyrites, and five to seven molecules with zinc blende.

This calculation does not consider the fact that the adsorbed surface is actually much larger than the calculated surface of particles due to possible rupture of the adsorbed surface. Also, a quantitative adsorption has been assumed, while from these determinations it follows that in very dilute oleic acid solutions the adsorption was relatively less than in concentrated solutions. Adsorption of oleic acid at the boundary surfaces of air bubbles was not accounted for. The stability of three-phase foam systems is a function of the foaming agent or stabilizer, that is, the power of adhesion between solid particles and air bubbles is determined by the adsorption layer. In order to render three-phase foam systems stable, the thickness of the solid layer or the oleic acid concentration should be such that the surface of the solid phase is covered with an oleic acid layer; this surface layer has none of the properties of oleic acid as a whole. Since the thickness of the layer considered was less than four molecules in diameter, the probability of a monomolecular layer was assumed. Beyond the optimum thickness, the bond between solid particles and air bubbles is weakened and the stability of the system decreased. Freundlich (15), discussing the action of solids upon foams, explains the resistance ability of the foam structure against solids as follows: When a solid is wetted by such solutions as soaps and saponin, it is "sucked" into the edge canals which are rich in liquid without destroying the structure of the foam externally.

Bartsch has defined conditions for the stability of a foam, taking into consideration the orientation theory of Langmuir (31) and Harkins (21).

The orientation theory postulates that molecules in the interface layer assume a definite direction. The atomic groups (carboxyl and oxyamido) of a molecule rich in residual valences are so placed that an almost complete saturation occurs in the boundary. When the boundary is not saturated by any residual valences, then the molecule directs the most saturated atomic group to this boundary, that is, the carboxyl group of oleic acid is directed to the solid phase, while the methyl group is directed towards the outside. When a methyl group comes in contact with a water–air boundary, it displaces the water molecules from the boundary layer because the interfacial surface tension in the presence of the methyl group is decreased, i.e., the water molecules are subjected to the expelling influence of the carboxyl group when competing for the surface of the solid phase.

The energy of the interface has a tendency to reach the lowest possible value, and this is the force which causes cohesion of solid particles to air bubbles. When only one molecular layer of oleic acid is present between air bubbles and solid particles, the intensity of adhesion is produced by the stronger forces existing between the residual valences of the solid phase surface and the forces of the carboxyl groups of the oleic acid. The latter forces are essentially greater than the forces of cohesion acting between the oleic acid molecules, as shown by Harkins. In the case of octane, the entrance of an oxygen atom into the molecule increases its cohesion up to 2 per cent, while the adhesion to water increases the cohesion up to 65 per cent. But the oleic acid is adsorbed not only by the solid phase, but also by the water–air boundary, depending upon which of the boundaries the oleic acid molecules have been previously adsorbed or, in other words, upon the rate of adsorption for the two boundaries. In the case of high oleic acid concentrations which are sufficient to surround gas bubbles as well as solid particles with an oleic acid layer, a certain attraction is always observed. Bartsch explained this as follows: In shaking an oleic acid emulsion with air in the presence of solid particles, the water–air boundary is always renewed. The rate of adsorption of the water–air interface and the rate with which an oleic acid droplet spreads upon the surface of a gas bubble is less than that of the adsorption by the solid phase.

Langmuir's conception regarding spreading, in this case, is based on the attraction existing between carboxyl groups and the molecules of the surface of the water or the surface of the solid phase. This attraction for the surface of a solid phase is greater than that for the surface of water, because the water molecules are displaced by solid particles wetted by oleic acid. The difference between the rate of adsorption and the rate of spreading of the oleic acid at the boundaries is due to the fact that even at higher concentrations of oleic acid the water–air boundary is not completely covered with a closed oleic acid layer, so that there will always exist a possibility for the formation of gas bubble complexes and solid particles. A gas, a liquid, and solid particles, held together by oriented oleic acid layers, comprise stable foams.

A monomolecular layer of oriented oleic acid molecules binds the aqueous solution to the gas and the solid surface, as well as the gas to the solid surface. The relation between the thickness of the interface layer and the stability of a foam, according to the orientation theory, may be described thus: As a result of the tendency of the free energy of the interface to acquire the lowest possible value in the case of low concentrations, the intensity of adhesion between solid particles and gas bubbles decreases with a decrease in the number of molecules of the foamer or stabilizer inducing adhesion. The intensity of adhesion between solid particles and gas bubbles is due to saturation of groups of molecules of the stabilizer rich in residual valences. These valences have their origin in the boundaries of the solid phase, as well as in a decrease in surface tension produced by saturated groups of substances in the gas–liquid boundaries.

In the case of high concentrations exceeding the optimum conditions of a state of permanency, the intensity of adhesion is the resultant of cohesion existing between molecules of the foamer in the adsorbed layer which, in this case, is made up of a considerable number of layers of molecules of the adsorbed substance.

The influence of cohesion becomes more marked the greater the number of layers of molecules. Orientation requires unsymmetrical molecules; for the most stable form of a system, it is necessary that it give the lowest free energy. Therefore the molecules orient themselves in the interface so that the paraffin hydrocarbon chain remains in the oil, while the active polar group (COOH), which exercises the greatest electromagnetic force, is in the water.

At the surface of the solid phase the molecules of water are subjected to the displacing influence of carboxyl groups; at the water–air boundary, the displacing influence of methyl groups towards oleic acid is effected.

C. CONCLUSIONS

1. Foams are labile formations with kinetic resistance lacking.
2. A dynamic, not a static, equilibrium is characteristic of foam systems. A great surface increase in foam formation counteracts stability with a decrease in surface tension.
3. The nature of the components participating in a system determines foam stability; lyophilic foams are more stable than lyophobic.
4. The rate of adsorption in the boundary accounts for the stability of foams.
5. Some ions may produce a considerable increase in the stability of foam systems, increasing the dispersion of the gas phase, while other ions act as peptizing agents.
6. For solid foamers, foam stability increases with the degree of dispersion.
7. High concentrations of substances added to increase the viscosity of a system increase its permanency.
8. Certain substances possess the ability to displace foamers from the interface.
9. Certain substances, such as glycerol, have a greater influence in the

production of soft and flexible skins than on viscosity. Elastic foams composed of large-sized bubbles are considered more stable than those of small-sized bubbles; this is not in alignment with other colloidal systems.

10. Electrostatic and capillary forces are involved in maintaining the stability of a foam.

11. The relation between the thickness of the interfacial layer and stability is analogous to that of emulsion systems. The Langmuir-Harkins orientation theory is applicable to foam systems.

IV. Transition to the Unstable State

A. FORCES ACTING IN THE THINNING OF A FILM

The interior of films composing foams is subjected to a continuous diminution in thickness by internal currents due to gravity and suction at the edges. The weight of the lamina has the tendency to make it thinner by forcing the molecules to slip continuously from the top to the bottom of the bubble. On the other hand, the liquid between two surface skins of a lamina moves upwards very slowly following the force of gravitation. The friction is great because, according to Poiseuille's law, the speed with which a liquid moves in a capillary is proportional to the fourth power of the radius and is, therefore, extremely small in such a small cross section.

Liquids behave differently. Gibbs (16) assumed that the motion of the liquid through which a bubble of air is rising is similar to that of a liquid running out from between two surfaces. This motion of the liquid may be greatly retarded by its viscosity as soon as the space between the two surfaces is reduced to the thickness of a lamina. The effect of an increase of the surfaces in increasing their tension becomes greater and more permanent as the quantity of liquid available for supplying the substances forming the increased surfaces diminishes. Gibbs gives a rough estimate of the amount of motion possible in the interior of a liquid lamina with respect to its exterior by calculating the descent of water between parallel vertical planes when the motion of water is reduced to zero. He uses the coefficient of viscosity determined by Helmholtz and Piotrowsky (22) and obtains $V = 581D^2$ where V denotes the mean velocity of water expressed in millimeters per second and D denotes the distance in millimeters between the fixed planes, which is supposed to be very small in proportion to their other dimensions. For the same temperature, the descent of water in long capillary tubes is $V = 337D^2$ and for descent between parallel planes it is equivalent to $V = 899D^2$. Gibbs draws the conclusion that in a film of a liquid which has a viscosity and a specific gravity not very different from that of water, the mean velocity of the interior relative to the surfaces will probably not exceed $1000D^2$. This is a velocity of 1 mm. per second for a thickness of 0.1 mm., 0.6 mm. per minute for a thickness of 0.001 mm., corresponding to the interference light of red of the fifth order in a film of water, and 0.036 mm. per hour for a thickness of 0.0001 mm., corresponding to white of the first order. Such a small internal current is evidently consistent with great persistence of the film, especially in those cases where the film can exist in a state of the greatest tenuity. On the other hand, Gibbs states that the above equations give so large a value of V for a thickness of 1 mm. or 0.1 mm., that a film evidently can be formed without drawing up any great weight of liquid, and any such thicknesses as these can have only a momentary existence.

Besides the action of gravity on the interior of a film, there is another cause producing changes, namely, the edge where the film terminates. At such an edge, there is generally present a liquid mass continuous in phase with the interior of the film bounded by concave surfaces. The pressure at the edge is, therefore, less than that in the interior of the lamina. Thus the liquid exerts a strong suction upon the interior of the lamina by which its thickness is rapidly reduced. Unless the lamina is very viscous, its decrease in thickness near the edge causes a rapid upward current on each side, while the central portion slowly descends. These processes rapidly reduce the thickness of the film. The volatility of the principal component is another example of the downward tendency of the interior of the film.

If in the case of a film of soap and water the humidity of the surrounding atmosphere is such that the vapor pressure of water at a level between the top and the bottom of the film has the same value in the atmosphere as in the film, then evaporation takes place in the upper portions and condensation in the lower portions. These processes occasion currents of diffusion, the effect of which is to carry the moisture downward. In the event the vapor pressure of water in the atmosphere differs little from that in the film, the processes described would not be sufficiently rapid to be of importance. But in the case of a film of soap and water in a dry atmosphere, or a film of soap and water with glycerol in a moist atmosphere, the effect of evaporation or condensation is not to be slighted. In the first case, a decrease in the thickness of the film is accelerated; in the second, it is retarded. In the case of a film containing glycerol, it is to be expected that the condensed water will not replace the fluid carried down by the internal current, but that a combination of these two processes will tend to remove the glycerol from the film. When a component which greatly diminishes the tension of a film is volatile, the effect of evaporation and condensation may be considerable, even when the mean value of the vapor pressure for that component is the same in the film as in the surrounding atmosphere. Gibbs illustrates this by using two components, S_1 and S_2, and states that the vapor pressure in a film must vary with the weight Z, since surface tension varies, and these variations very nearly satisfy the equation:

$$\gamma_1 \frac{d\mu}{dZ} + \gamma_2 \frac{d\mu_2}{dZ} = 0$$

γ_1 and γ_2 denoting the densities of the components S_1 and S_2 in the interior of a film. The variation of the potential of S_2 as we pass from one level to another is, therefore, as much more rapid than that of S_1 as its density in the interior of the film is less. If the resistances restraining evaporation, transmission through the atmosphere, and condensation of the two substances are the same, then these processes will proceed more rapidly with respect to S_2, and the values of $\frac{d\mu}{dZ}$ and $\frac{d\mu_2}{dZ}$ will have opposite signs, the tendency of S_1 being to pass downward and that of S_2 to pass upward. Moreover, the evaporation or condensation of S_2 will produce a much greater effect than evaporation or condensation of the same quantity of S_1. If condensation of S_2 takes place at the top of the film, it will cause a decrease in surface tension and an expansion in that part of the film by which its thickness is reduced as in evaporation of S_1 (16).

B. FACTORS INVOLVED IN THE TRANSITION TO THE UNSTABLE STATE

Thus the general conditions of the persistence of a liquid lamina are such that the substance which causes a decrease in surface tension in the lower parts of the film must not be volatile. Volatility influences rupture, for it is understood that when superficial molecules are lost by evaporation, their intrinsic cohesion must have been very small. In spite of the mobility of the superficial layers, little force is necessary to produce rupture; motion (evaporation) in the external molecules favors rupture. Plateau, in his theory on foams, assumed that in order for a liquid to be able to form bubbles, develop a large film and yet be resistant, it is necessary that the viscosity of the superficial layers of the film be sufficiently dense for thinning to occur slowly. But, on the other hand, it is also necessary that the surface tension be relatively weak so that it cannot overcome the opposite resistance of viscosity. Liquids having a high superficial viscosity and a relatively strong surface tension at the same time do not form bubbles. Liquids with a very low superficial viscosity do not form bubbles because the films surrounding them may become extremely thin in a short time, and an external or internal factor may break them. The chances for rupture are considerably less for a liquid having a low viscosity, as the bubbles are larger.

Plateau's principles further indicate that the superficial layer of liquids has a viscosity independent of the interior mass. In certain liquids, the superficial viscosity is greater than the internal viscosity, and sometimes to a considerable extent as, for example, in water and in a solution of saponin. In other liquids, on the contrary, the superficial viscosity is weaker than the internal viscosity, as in the case of turpentine and alcohol. The formation of a lamina is the result of cohesion and viscosity of a liquid. When a lamina develops it progresses in this manner because it is pushed upwards continuously by the air; hence it continues to rise. On the other hand, the liquid to which its edges are attracted cannot follow the lamina because of its weight. Therefore this liquid remains behind, but cohesion and viscosity interfere so that no rupture occurs between the lamina formed and the surrounding liquid, the lamina growing until the action exerted upon the outer part of the air bubble has produced its effect. Changes in physical conditions, such as an increase in the temperature of the liquid decreasing capillary pressure, cause the lamina to collapse under a smaller weight. The foam duration of a 0.05 molar aqueous solution of isoamyl alcohol at 50°C. was found by Bartsch to be 32 per cent lower than that at 18°C.

When the superficial layers have a very high viscosity, molecular motion is difficult, with no changes occurring in the film before it is affected by surface tension. Surface tension, when sufficiently energetic, disrupts the film. If a bubble is formed from a glycerol solution and expanded, it gradually changes in thickness before it ruptures. These gradual changes in thickness are visible macroscopically, as indicated by the coloration of the film. In a glycerol solution, the course in color change is reversed, that is, from red to green of the last order before rupture, owing to the fact that glycerol adsorbs moisture from the air. The action of weight tends to make the film thinner, adsorption on the contrary having a tendency to make it thicker. The course of color change shows that thinning has at first the greatest effect, but that later thickening dominates. There is an interval in the existence of a bubble where these two factors are counterbalanced, that is, a period in which the film gains as much as it loses. In case a glycerol solution has a density not exceeding 1.1, it undergoes only a small decrease in density compensated by an increase in fluidity as a result of dilution with water. Changes in density are not the principal reason for this thinning.

When the film has retained a large proportion of water, the relation between superficial viscosity and surface tension must be sufficiently great to make rupture difficult. On the other hand, because of continued adsorption of water vapor, the film should not become thicker in any phase of its life. These two factors constitute the resistance of the bubble to rupture. Furthermore, if the ratio between the superficial viscosity and the surface tension increases, but not in proportion with viscosity, it becomes insufficient to maintain permanency and the bubbles of the foam system collapse. This relation was pointed out by Plateau's (44) experiments (table 4).

The thinning of a film may be due to small concave surfaces formed along its contour. Thinning is slower for the same contour if the film occupies a larger surface. In the case of equal surfaces, thinning is less. This thinning rate increases with the diameter, but this is not the only factor involved in rupture, because if it were, the resistance of bubbles would increase with size. Usually these two influences compensate each other. A film of a given dimension has the greatest resistance to rupture when it is attached by its contour horizontally in a plane free from evaporation, agitation of air, or vibrations produced by the liquid. Two opposite forces act in a bubble, one centripetal, situated in the colorless part of the film, the other centrifugal, residing in the colored portion of the film with a maximum in the center corresponding to the so-called "black spot."[2] But apart from any action of the atmosphere, the interior of a fluid film is generally subjected to a continuous diminution in thickness by the internal current due to gravity and suction at the edges; sooner or later the interior ceases to possess the properties of matter as a whole. The film then becomes unstable with respect to the thinnest parts, which tend to become still thinner, owing to an apparent attraction between the surfaces of the film, discernible at its extremities, but becoming obvious when the thickness of the film is sufficiently reduced.

TABLE 4

Plateau's experiments

SUBSTANCE	SUPERFICIAL VISCOSITY	FILM TENSION	VISCOSITY-TENSION RELATION
Water	100.00	14.60	6.85
Glycerol	60.42	8.00	7.55
Saturated solution of sodium carbonate	91.14	8.56	10.65
Saturated solution of potassium nitrate	96.35	11.22	8.59
Saturated solution of calcium chloride	90.62	11.06	8.19
Marceille soap solution, 1/40	94.79	5.64	16.81
Domestic soap solution, 1/30	96.35	6.44	14.96
Potassium colophane solution (resin soap obtained by distillation of turpentine)	84.89	7.68	11.05
Saponin solution, 1/100	Extremely high	8.74	Very high (not determined)
Albumin solution	Identical	11.42	Identical

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[2] The black spots never have a thickness (20–40mμ) corresponding to the gray of the first order. The smallest thickness ever determined for these black spots was 100mμ (white of the first order); ordinarily, colors of higher orders are observed (300mμ).

Rupture of a film for many liquids cannot always be determined because it is rather sudden, and the intermediate phases of rupture cannot always be observed. However, there are methods for determining the thinning of laminae and for measuring the limiting thickness, which is a measure of the stability of films composing a foam: (1) by tracing the causes of thinning—gravity and surface tension, and (2) by observing the decrease in thickness produced by a centrifugal force, as shown by Rickenbacher (55).

Upon a drum rotated around a vertical axis, Rickenbacher spread a film in a horizontal plane and observed the appearance of Newtonian colors, which served as a measure for the decrease in thickness. (The Newtonian interference colors depend upon the interference of light reflected from the anterior and posterior surfaces of the laminae.) By a comparison of the colors observed with Boys' (6) table of colors, the apparent thickness of the lamina with an angle of incidence may be determined (the more light reflected, the greater the angle of incidence). Boys' table of factors may also be used in converting apparent thickness into actual thickness.

The process of thinning may be observed to a limited extent in soap-water films. It is apparent that a film whose coloration approaches black exhibits marked instability. The continuous change in color is interrupted only when the black spots make their appearance, spreading rapidly. Decomposition of soap solutions, rendering them opaque, is another reason for film rupture. Precipitation, not an expansion of the film, occurs during the formation of these black spots, and may be attributed to the film's greater thickness at their edge. Black spots apparently are many times thicker than the portion of the film from which they are formed. If the formation of black spots were due to an expansion of the film, it is evident that they would not be present. The thickening of the edge of the film cannot be accounted for by contraction. Expansion of the upper part of the film and contraction of the lower and thicker part would be resisted less by viscosity and favored more by gravity than such expansions and contractions producing the phenomenon described. A rapid formation of a thin spot by an internal current would induce an accumulation at the edge of the material forming the interior of the film.

Van der Willigen (70) states that films of alkali solutions are rather unstable because the black zone is formed from the alkali portion of the soap. However, Plateau believes it more probable that soap itself tends to be removed from the solution and out of the colored part of the film. In a much more concentrated solution, it forms the black zone. This opinion is based on Newton's experiments, which proved that dark blue always precedes black and is observed only when the solution contains a high proportion of soap. This led Plateau to assume that the difference in composition between the black zone and other parts of the film is small and the decrease in thickness gradual. The exploding force of a bubble is more intense the greater the proportion of water because the bubble bursts sooner, disintegrating its components, while, at the same time, the force of contraction has been weakened to the same extent. Conversely, the more soap present the less the intensity and the more energetic the force of contraction. This is to be doubted, because the force of contraction is surface tension, which decreases on increase in the proportion of soap. Leidenfrost (32) assumed as a consequence, therefore, that the force of rupture originates in water and the force of contraction in soap, so that the resistance of the bubbles varies with the concentration of the soap. Gibbs (16) pointed out that the retardation of the process by which films grow thinner cannot be accounted for in the formation of black spots, but may be attributed to a passive resistance to the motion due to the very viscous or gelatinous condition of the film. Also, it is unlikely that the formation of a stable film would occur without the support of such a resistance when rendered unstable during the same process by the precipitation of its mass. On the other hand, gelatinous properties are marked in soap solutions containing more soap than the amount required for the formation of films. This is true to a remarkable degree in saponin solutions. In an ordinary soap solution, however, no superficial viscosity greater than that of pure water was found (44). The resistance to an internal current is not measured by the resistance to motion, and it is doubtful whether a retardation of the tendency toward an internal current between elements adjacent to a black spot, changing slightly in thickness with time, may prevent rupture of the film (16). In a thick film the increase in surface tension with expansion necessary for the stability of the film is due to the presence of an excess of soap, or its components, at the surface as compared with the interior of the film.

C. CONCLUSIONS

1. A film undergoes continuous decrease in thickness before its collapse. The thinning effect is produced by the weight of the lamina, as well as by the difference in the pressure at the terminal edge of the film and its interior.
2. Evaporation and condensation processes influence the transition to the unstable state, depending on the volatility of the components decreasing surface tension. Rupture is facilitated by volatility.
3. Decrease in the thickness of a film is accelerated or retarded, depending on whether the film is in a dry or a moist atmosphere.
4. An increase in temperature, which diminishes cohesion and capillary pressure, assists in the collapse of foam under a smaller weight.
5. The superficial viscosity of a film must be sufficiently high to make thinning of the film slow.

6. The surface tension should be relatively weak, so as not to overcome the opposing resistance of viscosity.
7. The ratio between superficial viscosity and surface tension is Plateau's criterion for the unstable state. When the ratio is larger and not proportional to viscosity, foam bubbles collapse.
8. Two forces act in a bubble—centripetal and centrifugal—with the centrifugal force located in the colored portion of the film and concentrated in the "black spot."
9. The intensity of rupture of a bubble depends on the concentration of soap.

V. Foam Prevention

A. FACTORS INFLUENCING FOAM PREVENTION

In many industries foaming of liquids may or may not be desirable. As a matter of fact, in the heat treatment of certain liquids such as emulsified oils, foaming is a highly undesirable effect, and a number of methods are in use to prevent its taking place. In systems which foam, the general method for breaking or preventing the formation of foam is to have a superheating system above the evaporating surface of the liquid.

Pressure and high temperature reduce the tendency of liquid systems to foam. The lack of vapor space prevents substantial foam formation, as found in dehydrating emulsified crude oils (5). The properties of emulsified crude oils with respect to foaming are not additive. Intensity and persistency in foaming of emulsified oils to be dehydrated is decided by the nature of the oil. Foaming and the evaporation of water from the emulsified oil are markedly influenced by certain substances, such as gasoline. The foaming of emulsified oil increases as a function of the depth of the oil in the container, reaching its maximum at a definite temperature. Superheating and foaming occurring in the dehydration of emulsified oils produce evidence for the existence of a self-cooling effect.

Foaming of liquids often occurs during vacuum distillation. Jetting heated oil aids particularly in the dehydration of foaming oils (45). Small jets of emulsified oil are forced against a heated body beneath the surface of the liquid. Foam may be broken by passing it through a series of heated double grating plates (28). When passing the liquid to be distilled over a series of vertical plates, a countercurrent of the vapor prevents foaming (60). Foaming during steam distillation may be prevented by the addition of substances acting as defoamers. In most cases substances used in practice prevent or diminish foaming in a particular operation and are not universally applicable. The addition of many organic compounds to a foam made with a glue solution showed that in general fatty acids had a

TABLE 5

Examples of desirable foaming

USE	FOAM AGENTS	REMARKS
Flotation process	Amyl alcohol, Cresol, Xanthogenate } foamers Oleic acid, Paraffin oil, Naphthylamine, Xylidine } "collectors" adsorbed by hydrophobic ore powder	Ore dispersed in water is replaced by substances suitable for foam formation; foam originates by blowing in air Hydrophobic ore particles not readily wetted adhere to the foam laminae By skimming off foam, the ore is separated from the hydrophilic admixture and the thoroughly wetted quartz and feldspar not incorporated in the foam, together with the aqueous phase, sink to the bottom
Cleansing action of soap	Dirt particles	The dirt particles are carried by a hydrophobic skin in the interface as a result of emulsification, and are incorporated in the hydrophilic phase of the foam
Manufacture of beer, lemonade, etc.	Albumin Hop resins Saponin	The stability of a foam is a function of the fermentation process. It is assumed that acids originating in the fermentation process precipitate albumins and resins
Fire extinguishers	Solid particles (stabilizer)	A burning oil surface is extinguished by covering it with carbon dioxide and air containing foam; the foam contains in its laminae solid particles (stabilizer) separating the burning oil from the action of air. This action is similar to that of sand

greater effect upon the destruction of foam than the corresponding alcohols (38). No relation was found between the surface tension of the liquid and its ability to destroy foam, but in an homologous series the preventive effect appeared to increase with the molecular weight of the compound. With an increase in the concentration of the glue, the foaming power passed through a maximum. Certain mixtures were recommended for the prevention of foam; a mixture of linseed oil and alkali proved very effective. Petroleum, fat, milk, peanut oil, whale oil, oil of cloves, and various vegetable oils were found to decrease foaming in practice. Removal of sludge has been very often proposed to inhibit foaming. The addition of lime to maintain the pH above the neutral point is also a means of preventing foam formation. Small amounts of chlorine added to sewage reduce its tendency to foam.

TABLE 6

Examples of undesirable foaming

PROCESSES	FOAMING AGENTS	FOAM PREVENTERS	REMARKS
Paper production	Proteins Gelatin Dextrin Casein	Petroleum Fat Milk Peanut oil Oil of cloves Vegetable oils Alcohols of the fatty acid series	
Heat dehydration of crude oils	Introduction of steam into an emulsified oil undergoing dehydration, causing foaming	A mixture of linseed oil and alkali acts effectively in the prevention of foams	In the homologous series, the preventive effect increases with the molecular weight of the compound used
Heat dehydration of tars			Foaming in tars may occur when they contain less than 1 per cent of water

B. EXAMPLES OF DESIRABLE AND UNDESIRABLE FOAMING

Typical examples of the occurrence of desirable and undesirable foaming systems are illustrated in tables 5 and 6, respectively.

VI. SUMMARY

Foams are labile formations. From a thermodynamic standpoint, they are produced with a great surface increase, and this increase acts against the tendency of the system to reach a stable state by diminution of the surface. Small surface tension combined with small vapor pressure characterizes a foam agent. Only capillary-active organic substances promote foam formation, because only liquids containing such substances fulfill these conditions. Concentration of the capillary-active substance used as a foam agent is of great importance. A decrease in tension and foam formation acts parallel only at certain concentration values specific for each capillary substance used. Foam formation ability decreases parallel with a decrease in surface activity of the component dissolved in water. The decrease in solubility limits the increase in surface activity. The intermediate members of the homologous series show the most suitable relation between solubility and surface activity (considerable solubility and at the same time a high surface activity). The influence of solubility itself is well expressed. An increase in solubility increases the foam formation ability. Surface tension changes cause adsorption, resulting in a Gibbs interface layer. The interface layer in foams is made up of various kinds of molecules. There is no foam without a heterogeneous interface layer, and homogeneous liquids are unable to produce stable foams. The purely molecularly dispersed members of an homologous series allow a greater heterogeneity than the partially colloidally dissolved members. Solutions of surface-active substances foam better the more abrupt the concentration drop between the Gibbs layer and the solution.

Spreading is also a factor to be considered in foam formation. The rate of spreading is not parallel with the rate of surface increase in the formation of homogeneous layers, and the foam walls consist of heterogeneous layers.

The stability of foam systems is usually not high and is expressed in seconds of duration, although sometimes it reaches several days. Permanency may be increased under certain conditions. The coalescence of bubbles in a foam may be prevented by the addition of substances increasing the viscosity or rendering a certain elasticity which softens the skins of the interface. Foams may be classified as lyophilic and lyophobic with respect to their relation to electrolytes. Lyophilic foams have marked properties, such as viscosity and elasticity, and the influence of electrolytes on them is very small. Lyophobic foams are more stable and therefore less sensitive to electrolytes. Diminution of interfacial surface tension is one of the factors contributing to the stability of a foam system. Besides protective colloids, solids prevent coalescence of foam bubbles, maintaining a permanent foam system. The stabilization action of a solid in foam systems depends upon the degree of dispersion of the solid and its nature, affinity, and concentration. The ability of a solid to wet is of great importance. Those substances less wetted by water adsorb the capillary-active substance from the aqueous solution forming the Gibbs interface layer. A relation exists between the ability to wet, adsorption, and flotation.

Changes occurring in the foam system and leading to rupture of the interface film or to its gradual thinning induce an unstable condition. Continuous diminution of the thickness of the interface film by internal currents is due to gravity and strong suction at the edges of the film. The effects of the motion of external molecules, evaporation, and condensation are important. Volatility influences the rupture of the superficial molecules of the film which are readily lost because of diminution in cohesion due to evaporation. A viscosity strong enough to slow down the thinning of the film prevents coalescence of bubbles. An increase in the temperature of a foaming liquid diminishes cohesion and also diminishes capillary pressure so that bubbles collapse under a smaller weight. The relation between superficial viscosity and surface tension should be large enough to make the rupture of the film difficult. The film is subjected to two different actions: (1) weight, which has a tendency to make it thinner, and (2) adsorption which, on the contrary, tends to make it thicker. Where two forces counterbalance, an equilibrium of the foam is reached. Foam systems present a typical case of a dynamic and not a static equilibrium. In the case of a solid used as a stabilizer, the dynamic equilibrium established between the rate of formation of the adsorbed layers of the foam-forming agent, or stabilizer, at the solid–liquid boundary on the one hand, and the rate of such layer formation at the gas–liquid interface on the other hand, determines to a certain extent the stability of a three-phase foam system. Small solid particles may contribute to the stabilization of a froth or foam, as in the case of mineralized froth, or in the ore flotation process, by preferential aggregation in the interface between two phases. Gas bubbles adhere to the solid particles in spite of the electrostatic repulsion of the components. The attraction between components of a foam system should be ascribed to more powerful capillary forces rather than to electrostatic forces. The function of capillary force is to separate the intermediate parts between two bubbles and to prevent coalescence where diminution of the surface occurs.

The adsorption layer in the interface evidently plays a most significant part in the stabilization of foam systems. In calculating the thickness of this layer, Bartsch proved that the maximum stability of these systems corresponds to a unimolecular film. An attempt has been made to explain the relation between the thickness of the interface layer and the stability of a foam system based on the Langmuir-Harkins theory of the fine structure of the boundary layers for those concentrations of foam-forming agents or stabilizers which lead to permanent foam systems. The intensity of adhesion between solid particles and gas bubbles is caused by the saturation of groups of molecules of the stabilizer rich in residual valences. These residual valences originate in the boundaries of the solid phase and are the result of the influence of the most saturated group of molecules of these substances, decreasing the surface tension at the gas–liquid boundaries, and the free boundary energy acquiring the smallest possible value. For small concentrations, the intensity of adhesion between solid particles and gas bubbles decreases with a decrease in the number of molecules of the foam agent or stabilizer causing adhesion.

At concentrations exceeding the condition of permanency, the adhesion between solid particles and gas bubbles occurs only when the dynamic equilibrium permits the formation of gas–liquid boundaries partially free from adsorbed molecules of the foam-forming agent or stabilizer.

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