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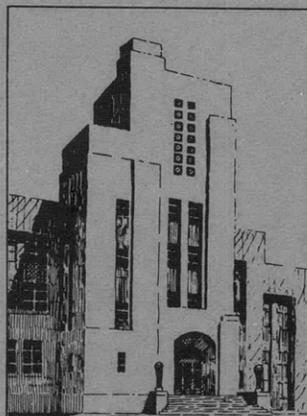
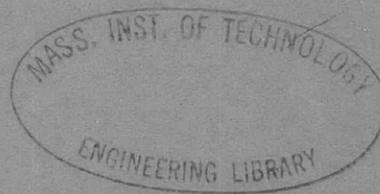
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# THE DAVID W. TAYLOR MODEL BASIN

UNITED STATES NAVY

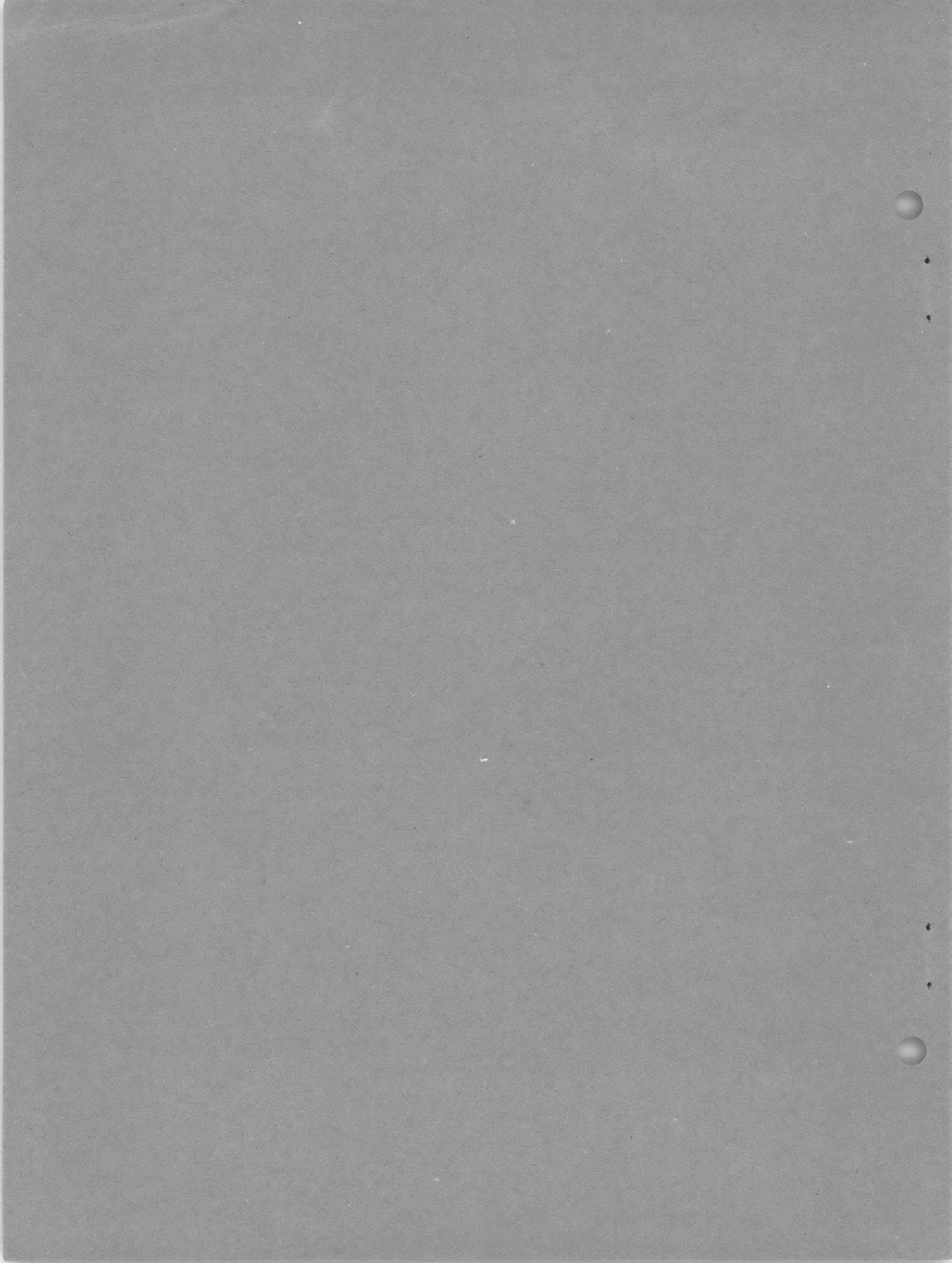
THE SIZE OF GAS BUBBLES IN LIQUIDS

- BY ROBERT SCHNURMANN -



MARCH 1943

TRANSLATIONS 110



THE SIZE OF GAS BUBBLES IN LIQUIDS

(DIE GRÖSSE VON GASBLASEN IN FLÜSSIGKEITEN)

by

Robert Schnurmann

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Translated by F.A. Raven

The David W. Taylor Model Basin  
Bureau of Ships  
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## THE SIZE OF GAS BUBBLES IN LIQUIDS

### ABSTRACT

The size of gas bubbles forced through a filter into a liquid depends on the nature of the liquid and is independent of the character of the filter.

The size of the bubble as a function of the viscosity of the liquid is shown for dielectric fluids, acids, bases, and salt solutions. The mechanism of macroscopic bubble formation is observed and considered.

In electrolytic solutions the additional factor of the electrostatic interaction of the charged gas bubbles is added to the effect of viscosity. This interaction permits determination of the order of magnitude of the concentrations of reversal of solutions whose viscosity does not perceptibly exceed that of water.

The experimental result permits interpretation of the scatterings obtained upon determination of the pore diameters of ceramic filters for various liquids by the air pressure method.

Applications for gas absorption by liquids, and flotation are discussed.

Two cases must be treated separately: 1. freely oscillating gas bubbles in the interior of the liquid, and 2. the formation of gas bubbles on the interfaces. The growth of freely moving gas bubbles in liquids supersaturated with the same gas has been investigated by Fricke (1),\* who found that the growth of the bubbles is a function of the supersaturation of the liquid by the gas and also of the original size.

Experiments by Coehn and Neumann (2) and by Kohlschütter (3) give information on the size of electrolytically developed gas bubbles where the interface is composed of the fluid in contact with metal. According to Coehn and Neumann the size of the gas bubbles depends upon the electric charge and the sign of the electrode. If the bubble and the electrode have the same sign the bubbles repel each other, and the bubbles are small. However, when the signs of the bubble and electrode are opposite, saturation occurs, the bubbles cling to the electrode; they grow and can reach diameters of several millimeters before their buoyancy overcomes the attractive force. In the electrostatic interaction between the electrode and the charged gas bubble, the effect of the liquid is determined only by the charge of the bubble which is a function of the nature of the liquid.

This is a problem of macroscopically visible gas bubbles. Kohlschütter's ultramicroscopic observations contribute to a knowledge of their origin. From copper sulfate solutions whose concentration is constantly below 0.01 normal, black copper can be formed on the cathode with platinum and copper electrodes. Accompanying this

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\* Numbers in parentheses indicate references on pages 16 and 17 of this translation.

colloidal copper, nebulous oxygen is released on the cathode. The ultramicroscopic tiny bubbles which form a zone parallel to and separate from the cathode, are negatively charged. Their origin on the cathode cannot be observed. The tiny bubbles are originally ultramicroscopically invisible and become visible only after many such small structures have coalesced. Owing to their negative charge they are immediately repelled by the cathode.

The macroscopic behavior of gas bubbles on the interface formed by liquid and metal without the action of an electric field is known from research by Coehn and Neumann. Gas bubbles which are electrostatically bound to an electrode and which have increased to observable size are not released from the electrode when the field is switched off. They even withstand violent shocks before they are torn loose. The bubbles subtract their own charge from the metal, leaving it with an equal, opposite charge which holds them fast.

The problem is whether the liquid/solid interface is definitive for the behavior of gas bubbles when a gas is forced through metallic or non-metallic jets into a liquid.

It has been observed in aquariums that in the fresh water basin gas bubbles rise which are of different size from those in the salt water tank, although both tanks are provided with the same jets through which the air is forced with the same pressure. Large bubbles rise in fresh water, small ones in salt water.

Kautsky and Thiele (4) used this phenomenon to produce nitrogen completely free from oxygen. They sought the conditions under which flask nitrogen, in which small amounts of oxygen are always mixed, would effervesce in extremely fine distribution through the absorption liquid. For this purpose the gas was forced through porous walls of clay, porcelain, or infusorial earth under a low excess-pressure into the absorption liquid, which was sodium hydrosulfite. It was essential for absorption, "that the little bubbles emanating from the porous walls be prevented from uniting into larger ones."

The electrostatic phenomena for gas bubbles in fluids, which were discovered and more closely examined by Coehn and his colleagues, were used to interpret the fine distribution of the gas. These investigators assumed equal charge of the gas bubbles\* and the porous wall to be requisite for the prevention of coalescence into larger bubbles. They selected a porous cell whose sign, determined by cataphoretic tests with concomitant suspension of the materials in question, corresponded to that of the gas bubbles. The latter is generally negative in alkaline liquids and positive in acids above a precisely defined concentration (5). Using sodium hydrosulfite, Kautsky and Thiele obtained an exceptionally fine distribution of the gas, and oxygen-free nitrogen with less than 0.0007 per cent oxygen.

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\* In the term "charge of the gas bubbles," chosen for brevity, that part of the boundary layer of the liquid surfaces which are adjacent to the interior of the liquid, is to be understood. Moreover, this charged layer determines the direction in which the gas bubble will move when electrophoresis occurs.

According to private reports, Coehn and Apel (6) orally explained that the electrostatic relationships cannot be made responsible for the size variations of the gas bubbles. Their experiments and those of the author, in which the gas is partly stirred into the liquid and partly forced into the liquid through porous bodies, allow several characteristics of the viscosity of the liquid under consideration to be recognized. Obviously the size of the gas bubbles in liquids depends on the capacity of many very small bubbles to coalesce, as Kautsky and Thiele already recognized.

Observations with water, alcohol, and water-alcohol mixtures appeared to indicate a method of explaining the nature of this interdependence. Air which was forced through entirely different types of filters, such as Pukallfilters, Ballonfilters (kaolin), carbon filters, glass filters and Berkefeldfilters, into distilled water, always produced large bubbles. Large bubbles were also produced when methyl alcohol or absolute alcohol was substituted for water. However, if a 45 per cent to 50 per cent ethyl alcohol solution was used, small bubbles resulted. These three observations strongly point to an interrelation of the phenomena or a connection of these phenomena with the viscosity of the liquid. The internal friction of water and alcohol is practically equal while that of a mixture of the two is greater and reaches its maximum at 45.57 per cent (7).

The problem of bubble size as a function of the nature of the liquid became especially acute when the pore diameters of ceramic filters were studied by the "pressure bubble method" (8). It was found that for air forced through filters saturated with various liquids, the calculated pore diameters scatter up to 100 per cent. It must be considered that the tiny air bubbles which are pressed through the individual pores are first invisible (sub-visible) and that only after many bubbles have become united is a bubble produced which is sufficiently large to be seen by the naked eye.

#### EXPERIMENTS

The viscosity curves of the systems composed of two substances, i.e., water-methyl alcohol, water-ethyl alcohol, and water-*n*-propyl alcohol, pass through maxima (9). To determine the curves which are derived from the size of the air bubbles in these systems a filter candle attached to a compressed air line is inserted into a vessel which contains the liquid system to be studied.\* The sizes of the bubbles, whose differences are very evident, are estimated and hence can only be qualitatively arranged in three separate divisions. These are small, medium, and large. The concept of small bubbles is applied to those whose diameter is somewhat less than 1 mm. Medium bubbles are those with the diameters between 1 mm and 2 mm, and large ones over 2 mm.

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\* In every case pressures used subsequently herein exceeded those necessary to cause the filter "to emit gas generally."

It was observed that air bubbles in  
 10 per cent alcohol were larger than in 90 per cent alcohol ( $\eta_{10\%} < \eta_{90\%}$ )  
 33 per cent alcohol were smaller than in 67 per cent alcohol ( $\eta_{33\%} > \eta_{67\%}$ )  
 0 per cent alcohol were larger than in 100 per cent alcohol ( $\eta_{0\%} < \eta_{100\%}$ ).

Whereas the viscosity curves of the three cited systems each composed of two substances show maxima, the curves for bubble size show minima at corresponding points and can be studied unaided.

TABLE 1\* METHYL ALCOHOL--WATER

Observation at 24.2 degrees C			Internal Friction at 25 degrees C	
Filter	Alcohol Content per cent	Bubble Size	Alcohol Content per cent	Internal Friction $\eta$
Glass	0	Large	0	0.00891
	20	Medium	20.74	0.01378
	40	Medium	37.82	0.01567
	80	Large	79.64	0.01003
	100	Large	100	0.005525

TABLE 2 ETHYL ALCOHOL--WATER

Observation at 24.2 degrees C			Internal Friction at 25 degrees C	
Filter	Alcohol Content per cent	Bubble Size	Alcohol Content per cent	Internal Friction $\eta$
Glass	0	Large	0	0.00891
	10	Medium	20.71	0.01829
	33	Medium	39.65	0.02343
	45	Small	45.57	0.02351
	50	Small		
	67	Medium	61.85	0.02173
	90	Medium	78.09	0.01804
	100	Large	100	0.01125

\* In this and following tables, the percentual viscosity data most closely associated with those chosen for observation were taken from Landolt-Börnstein-Roth-Scheel, "Tables."

TABLE 3 N-PROPYL ALCOHOL--WATER

Observation at 24 degrees C			Internal Friction at 25 degrees C	
Filter	Alcohol Content per cent	Bubble Size	Alcohol Content per cent	Internal Friction $\eta$
Glass	0	Large	0	0.00891
	25	Medium	28.62	0.02118
	60	Small	59.38	0.02652
	74	Medium	73.13	0.02509
	100	Medium	100	0.01936

The system composed of acetic acid and water likewise has a viscosity curve with a maximum. The latter is at 79.43 per cent acetic acid by volume. Table 4 shows a study of the bubble sizes.

Observations with various types of filters in the same liquid show that the nature of the filter does not affect the size of the bubbles.

TABLE 4 ACETIC ACID AND WATER

Observation at 24 degrees C			Internal Friction at 25 degrees C	
Filter Filter	Acetic Acid Content per cent	Bubble Size	Acetic Acid Content per cent	Internal Friction $\eta$
Glass	0	Large	0	0.00891
	78	Small	79.43	0.02403
	100	Large	100	0.01140

TABLE 5 SIZE OF BUBBLES WITH VARIOUS FILTERS

Filter	Liquid	Bubble Size	Temperature degrees C
Glass	Water	Large	20
Porcelain Earth	Water	Large	17
Carbon	Water	Large	20
Berkefeld	Water	Large	20
Glass	Isobutyl alcohol	Small	20
Porcelain Earth	Isobutyl alcohol	Small	17
Glass	Sodium Chloride Solution	Small	20
Carbon	Sodium Chloride Solution	Small	20

The non-dependence of the size of bubbles on the nature of the filter revealed in Table 5 suggests that the differences of the sizes of bubbles in various liquids must occur even if the air bubbles are introduced into the liquid without the aid of a filter. A method of doing this consists in allowing a liquid to escape from a nozzle. The jet entrains air and whirls it into a vessel filled with the same liquid.

TABLE 6 ENTRAINMENT OF AIR BY A JET OF LIQUID FLOWING FROM A METAL NOZZLE

Liquid	Bubble Size
Water	Large
Ethyl alcohol	Large
45 per cent Ethyl alcohol	Small
3 per cent Hydrogen Peroxide	Large
Saturated Sodium Chloride	Small

Admixture of air can also be accomplished by shaking a vessel filled with the liquid. The rough differences in the size of the bubbles are still visible in this case.

The size of the bubbles as a function of the viscosity of the fluid must be explained by the effect of temperature. Hence the size of the bubbles varies inversely as the viscosity.

TABLE 7 BUBBLE SIZE AS A FUNCTION OF TEMPERATURE

Filter	Liquid	Bubble Size	Temperature degrees C	Internal Friction $\eta$
Balloon	Water	Large	17	0.01
	Isobutyl alcohol	Small	17	0.04
Glass	Isobutyl alcohol	Small	20	0.04
Balloon	Isobutyl alcohol	Large	80	0.009
Berkefeld	40 per cent acetic acid	Medium	24	0.017 at 25 degrees C*
		Medium	29	0.015 at 30 degrees C*
		Medium	32	
		Medium	55	0.0089 at 55 degrees C*
		Large	65	
		Large	78	

\* For 38.91 per cent acetic acid by volume.

Table 8 shows that potassium hydroxide in even slight concentration (0.01 normal) decreases the size of the bubble, whereas dilute sulfuric acid (0.1 per cent) and dilute sodium chloride solution (0.1 per cent) cannot effect this change.

TABLE 8 EFFECT OF CONCENTRATION ON BUBBLE SIZE

Filter	Liquid	Concentration per cent	Bubble Size	Temperature degrees C	Internal Friction $\eta$
Glass	Potassium Hydroxide	very dilute	Small	20	
	Sodium Chloride	10	Small	24	0.01181*
	Sodium Chloride	5	Small	23	0.01078**
	Sodium Chloride	2.5	Small	23	
	Sodium Chloride	1	Medium	21	0.01009†
	Sodium Chloride	0.1	Large	21	
	Sulfuric Acid	10	Medium	25	
	Sulfuric Acid	5	Medium	25	
	Sulfuric Acid	1	Medium	25	
	Sulfuric Acid	0.1	Large	24	

\* At 20.46 degrees C.    \*\* At 20.22 degrees C.    † At 20.26 degrees C.

TABLE 9 EFFECT OF ACIDITY AND ALKALINITY ON BUBBLE SIZE

Filter	Liquid	Concentration	Bubble Size	Temperature degrees C	Internal Friction $\eta$
Glass	Sulfuric Acid	Concentrated	Small	25	0.235
	Hydrochloric Acid	Concentrated	Medium	25	
	Nitric Acid	Concentrated	Medium	25	0.01770*
	Nitric Acid	10 per cent	Medium	25	
	Ammonia	25 per cent	Medium	25	
	Ammonia	10 per cent	Medium	22	
	Lactic Acid	Concentrated	Large	18	0.4033**
	Lactic Acid	50 per cent	Medium	18	
	Lactic Acid	10 per cent	Medium	18	
	Lactic Acid	1 per cent	Small	18	
	Lactic Acid	0.1 per cent	Small	18	
	Lactic Acid	0.01 per cent	Small	18	
	Lactic Acid	0.001 per cent	Small	18	
	Lactic Acid	0.0001 per cent	Small	18	
	Potassium Hydroxide	very dilute	Small	20	

\* At 10 degrees C    \*\* At 25 degrees C

TABLE 10 BUBBLE SIZE IN VARIOUS SALT SOLUTIONS

Filter	Solution	Concentration		Bubble Size	Temperature degrees C	Internal Friction $\eta$
		Per Cent Solution	Normality			
Berkefeld	Sodium Chloride	10	1.71	Small	22	0.01181 at 20.46 degrees C 0.01078 at 20.22 degrees C
		5	0.85	Small	22	
		2.5	0.43	Small	22	
		1	0.17	Medium	22	0.01009 at 20.26 degrees C
		0.1	0.017	Large	22	
Berkefeld	Sodium Hydrosulfite	10	1.92	Small	22	
		5	0.96	Small	22	
		2.5	0.48	Small	22	
		1	0.192	Medium	22	
Berkefeld	Potassium Chloride	10	1.34	Small	22	0.01056 at 18 degrees C 0.010095
		5	0.67	Small	22	
		2.5	0.34	Medium	22	
		1	0.13	Medium	22	
		0.1	0.013	Large	22	
Berkefeld	Sodium Bromide	10	0.973	Small	23	
		5	0.49	Small	23	
		2.5	0.25	Medium	23	
		1	0.097	Medium	23	
		0.1	0.0097	Medium	23	
Berkefeld	Barium Chloride	9	0.863	Small	23	
		5	0.48	Small	23	
		2.5	0.24	Small	23	
		1	0.096	Medium	23	
		0.1	$9.6 \times 10^{-3}$	Medium	23	
		0.01	$9.6 \times 10^{-4}$	Large	23	
Berkefeld	Calcium Nitrate	10	0.847	Small	24	
		5	0.424	Small	24	
		2.5	0.212	Small	24	
		1	0.085	Medium	24	
		0.1	$8.5 \times 10^{-3}$	Medium	24	
		0.01	$8.5 \times 10^{-4}$	Medium	24	
		0.001	$8.5 \times 10^{-5}$	Large	24	
Berkefeld	Magnesium Sulfate	10	1.66	Small	23	
		5	0.83	Small	23	
		2.5	0.42	Small	23	
		1	0.17	Medium	23	
		0.1	0.017	Large	23	
Berkefeld	Aluminum Chloride	10	2.25	Small	22.5	
		5	1.13	Small	22.5	
		2.5	0.56	Small	22.5	
		1	0.23	Small	22.5	
		0.1	0.023	Small	22.5	
		0.01	$2.3 \times 10^{-3}$	Medium	22.5	
		10	$2.3 \times 10^{-4}$	Medium	22.5	
		10	$2.3 \times 10^{-6}$	Medium	22.5	
		10	$2.3 \times 10^{-6}$	Medium	22.5	
		10	$2.3 \times 10^{-7}$	Medium	22.5	
		to Large				
Berkefeld	Ferric Chloride	10	1.85	Small	23	
		5	0.93	Small	23	
		2.5	0.47	Small	23	
		1	0.19	Small	23	
		0.1	0.019	Small	23	
		0.01	$1.9 \times 10^{-3}$	Medium	23	
		10	$1.9 \times 10^{-4}$	Medium	23	
		10	$1.9 \times 10^{-5}$	Medium	23	
		10	$1.9 \times 10^{-6}$	Medium	23	
		10	$1.9 \times 10^{-7}$	Large	23	
Berkefeld	Thorium Nitrate	10	0.83	Small	20	
		5	0.42	Small	20	
		2.5	0.21	Small	20	
		1	0.083	Small	20	
		0.1	$8.3 \times 10^{-3}$	Small	20	
		0.01	$8.3 \times 10^{-4}$	Small	20	
		10	$8.3 \times 10^{-5}$	Medium	20	
		10	$8.3 \times 10^{-6}$	Medium	20	
		10	$8.3 \times 10^{-7}$	Medium	20	
		10	$8.3 \times 10^{-8}$	Medium	20	

The results summarized in Table 9, however, show that the basic or acidic nature of solutions does not primarily determine the size of the bubble.

It is striking, in Table 8, that a 10 per cent sodium chloride solution produces small bubbles, although its viscosity according to references contained in the literature is scarcely 20 per cent greater than that of water. Therefore, experiments were performed with various salt solutions; Table 10 gives the results.

To emphasize the secondary electrolytic effect, which will be further discussed, additional studies made on solutions of cane sugar and urea are included.

TABLE 11 BUBBLE SIZE IN SOLUTIONS OF CANE SUGAR AND UREA

Filter	Substance	Solution per cent	Bubble Size	Temperature degrees C	Internal Friction $\eta$
Berkefeld	Sugar	40	Medium	22	0.06004 at 20.23 degrees C
		20	Small	22	0.01910 at 20.04 degrees C
		10	Medium	22	0.01322 at 20.29 degrees C
		5	Medium	22	0.01127 at 20.29 degrees C
		1	Large	22	0.01031 at 20.0 degrees C
	Urea	10	Medium	23	
		5	Medium	23	
		2.5	Medium	23	
		1	Large	23	
		0.1	Large	23	

#### DISCUSSION OF EXPERIMENTAL RESULTS

Tests where air is not pressed through filters but carried along by a jet of liquid or stirred into the solution by shaking show that the size variations of gas bubbles in various liquids are not dependent upon the presence of a filter. They also show that the phenomenon depends upon the nature of the liquid and not on the effect which is produced by a filter in contact with a liquid.

Therefore, if the electrostatic effects of the filter wall can be disregarded when interpreting the phenomena, then the surface tension of the liquid and its internal friction are the two properties whose effects must be studied.

If the size of the bubbles depended upon the air/liquid interfacial tension, the smallest bubbles would necessarily be produced in water because of its great surface tension; in organic liquids, whose surface tension is considerably smaller than that of water, the bubbles would necessarily be larger than in water. However, observations with isobutyl alcohol show that this is not true.

Thus the process of visible formation is represented as follows. On 1 mm<sup>2</sup> (0.00155 square inch) of filter surface at an assumed average pore diameter of  $4\mu$ ,\*

\*  $\mu$  represents a micron, a millionth of a meter (0.000039 inch).

there are countless numbers of pores. The pores are saturated with liquid. Let the air pressure exerted upon one side of the filter be equally distributed over the pores. The columns of liquid in the pores are pressed downward and the menisci appear simultaneously at the orifices of the pores. The diameter of the menisci averages  $4\mu$ ; therefore, the original appearance cannot be observed with the naked eye. These invisible little bubbles impinge upon one another. A large number of them occasionally unite to form a visible bubble. The rapidity of this coalescence and the number of bubbles participating in it increase in direct ratio with the motility of the bubbles, that is, in inverse ratio with the viscosity of the liquid.

#### DIELECTRIC LIQUIDS

First the size of gas bubbles in dielectric liquids will be observed. Tables 1, 2, 3, and 4 show the agreement between minimum bubble size and concentration, for various pairs of liquids. The internal friction of the component liquids of each pair is of the same order of magnitude and attains a maximum at a definite ratio of the two phases.

Table 7, with isobutyl alcohol as an example at 80 degrees C, where its internal friction corresponds to that of water at room temperature, shows that the size of the bubble corresponds to that observed in water at room temperature.

Table 11 shows the size increase of gas bubbles in cane sugar and urea solutions as the viscosity decreases. The gas bubbles in the 40 per cent cane sugar solution are of medium size and in spite of the considerably larger viscosity compared to the 20 per cent solution, are no longer small. This fact explains the observation of bubble sizes in highly viscous liquids, for example, in a 10 per cent glacial acetic acid-collodion solution. In such a solution very large bubbles are produced, with an appendage by which they are inflated; see Figure 1. They detach themselves from the surface of the filter very slowly as very large bubbles and rise to the surface of the liquid where they form a foam consisting of large bubbles.

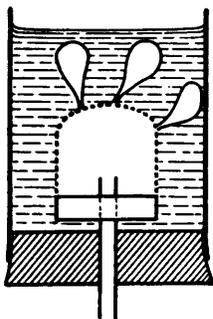


Figure 1

There is no noticeable tendency for these bubbles to unite. Parallel to the increase in viscosity, starting with the value where small bubbles are produced, highly viscous fluids likewise show increasing size of bubble. The division into three magnitudes, small, medium and large, is therefore restricted to the range where  $\eta$  equals 0.008 to 0.04.

Table 11, furthermore, gives an idea of the sensitivity of this qualitative method for the recognition of differences in viscosity. Experiments in other fields (10) show that cane sugar solutions, at least in concentrations above 0.5 Mol/liter, have a greater viscosity than urea solutions of equal concentration. A 20 per cent cane sugar solution corresponds to 0.58 Mol/liter, a 10 per cent urea solution to 1.66 Mol/liter. The bubbles are small in the sugar solution, large in

the urea solution. Whereas no large bubbles are produced in a cane sugar solution containing only 0.15 Mol/liter, such bubbles are produced in a urea solution containing only 0.17 Mol/liter.

A further observation on the variation of the size of the bubbles in the presence of ether vapor should be mentioned. Large bubbles are produced in water. If an open flask of ether is held near the surface of the water, the bubbles become smaller and are bunched in the middle of the vessel as they traverse the column of fluid. Their rise is accelerated. The ether vapor also produces a movement in the liquid without effervescing gas bubbles (11), which, similar to the camphor dance, is caused by the decrease in surface tension effected by the ether vapor at the points where it comes in contact with the liquid. This movement counteracts the gradual growth of the gas bubbles.

#### ELECTROLYTES

The data for electrolytes are contained in Tables 8, 9, and 10. In very dilute lactic acid as well as in very dilute potassium hydroxide small bubbles are produced. Concentrated lactic acid and concentrated sulfuric acid are far above the viscosity range herein treated.

The behavior of acidic, basic, and salt solutions is essentially different from that of dielectric liquids. This is particularly apparent in Table 10 for sodium chloride and potassium chloride. Although the viscosities of their 5 per cent and 10 per cent solutions are about the same as that of water, the bubbles in a 1 per cent solution are still of medium size and only become large in a 0.1 per cent solution. Here a secondary effect which is determined by the charge of the bubble is joined to that of viscosity. In pure water the gas bubbles are negatively charged. Additions of acids or bases decrease the charge, as Coehn and Mozer showed (5) by the effect of effervescence, and reduce the charge to zero at a definite concentration, i. e., the so-called "concentration of reversal." Further addition of acid produces a reversal of the sign. McTaggart (12) conceived an arrangement to study the charge of the bubble in the interior of the liquid and to test the effect of ions of different values. From McTaggart's measurements, Neumann (13) calculated that the concentration of reversal lies much lower than the concentration of reversal produced by the phenomenon of entrainment according to Mozer; for  $\text{Al}(\text{NO}_3)_3$ , for example, it is at  $1 \times 10^{-5}$  normal as contrasted to  $2 \times 10^{-2}$  normal according to Mozer.

The mechanism of the flaky precipitation of suspensions and emulsions depends both on the size of the gas bubbles and on the electric charge of the suspended or emulsified particles and upon the viscosity of the dispersing medium to the degree that an emulsifier is lacking. The difference between the two phenomena consists in the fact that for the flocculation of the brine particles electric neutralization is a prime requisite. The viscosity of the dispersing medium exerts a hindering effect in the latter process. The size of the gas bubbles, however, depends primarily on the

viscosity of the dispersing medium. Only in the case when the little bubbles are strongly charged electrically does the latter noticeably counteract coalescence if the viscosity of the electrolyte does not exceed that of water. The effect of surface tension is negligible in both cases.

Conditions in water constitute the point of departure for these observations. Bubbles in water are designated as large. Additions to water can increase its viscosity. As has been shown, the size of the bubbles is decreased by such additions, and the decrease is noticeable at even a small increase of viscosity. Additions of salt to water which produce an almost imperceptible increase of viscosity are sufficient to reverse the charge of the gas bubbles [ $10^{-5}$  normal  $\text{Al}(\text{NO}_3)_3$ ] and impart an observable positive charge to them. A considerable electrostatic repulsion of the bubbles of like charge is now superimposed on the vanishingly small retardation of the motility of the gas bubbles which is a hindrance to coalescence. If the latter (i.e., repulsion of like-charged bubbles) occurs in the size of the gas bubbles here observed, the concentration at which medium sized bubbles are formed from small ones and large from medium sized, must drop as the valence of the cations of the salt rises, when the viscosity of the liquids is practically constant. Table 12

TABLE 12 SALT CONCENTRATIONS AT WHICH BUBBLE SIZES CHANGE

Solution	Normality	Transition
Potassium Bromide	0.21	Small to Medium
Potassium Chloride	0.335	
Sodium Chloride	0.179	
Sodium Hydrosulfite	0.114	
Barium Chloride	0.094	
Calcium Nitrate	0.122	
Magnesium Sulfate	0.166	
Aluminum Chloride	0.002	
Ferric Chloride	0.0018	
Thorium Nitrate	0.00008	
Potassium Bromide	<0.008	Medium to Large
Potassium Chloride	0.013	
Sodium Chloride	0.017	
Sodium Hydrosulfite	not observed	
Barium Chloride	0.0009	
Calcium Nitrate	0.0001	
Magnesium Sulfate	0.016	
Aluminum Chloride	0.0000002	
Ferric Chloride	0.00000018	

shows the salt concentrations at which the transitions from small to medium bubbles and from medium to large bubbles occur.

From Table 12 it is evident that the electrostatic effect for molecules which break into two ions, i.e., transitions from medium to large size, is first perceived at relatively high concentrations; whereas, transitions from small to medium size first become clearly noticeable in lesser concentration for molecules breaking down into three and four ions. Above such concentrations, the viscosity becomes the predominating factor.\* The assumption that in dilute electrolytes of viscosity equal to that of water, the bubble charge is one of the determining factors of bubble size would require that at the "concentration of reversal" the bubble size should reach a maximum. This maximum value of the bubble size is larger than or at least equal to that in pure water and increases in the direction of smaller concentrations on continuation of the observations contained in Table 10. The effervescent effect for sulfuric acid gives the concentration of reversal  $2 \times 10^{-3}$  normal\*\* (5). The observations of the bubble size according to Table 13 result in a smaller value, i.e.,  $10^{-5}$  normal.\*\*

TABLE 13 EFFECT OF CONCENTRATION ON THE SIZE OF BUBBLES IN SULFURIC ACID

Filter	Substance	Concentration normality	Bubble Size	Temperature degrees C
Berkefeld	Sulfuric Acid	$10^{-1}$ normal	Large	30
		$10^{-2}$ normal	Large	30
		$10^{-3}$ normal	Large	30
		$10^{-4}$ normal	Large	30
		$10^{-5}$ normal	Very Large	30
		$10^{-6}$ normal	Large	30
		$10^{-7}$ normal	Large	30

The observations at low concentrations for several monovalent, bivalent, trivalent and quadrivalent salts are summarized in Table 14.\*

It may be concluded from Tables 13 and 14 that a decrease in the size of the bubbles will occur in a concentration increasing from zero for electrolytes whose dilute solutions differ but slightly in viscosity from water. This decrease is then followed, within the range of low concentrations, by an increase to a maximum from which point the bubble-size drops as the concentration rises. Table 15 summarizes the maximum bubble size contained in Tables 13 and 14.

\* Translator's Note: To show this graphically, data given in Table 14 of this paper have been plotted at the David W. Taylor Model Basin. The curves are given in Appendix 1.

\*\* The order of magnitude only can be considered reliable in these observations.

TABLE 14. VARIATION IN BUBBLE SIZE WITH CONCENTRATION OF ELECTROLYTES

Filter	Electrolyte	Concentration	Bubble Size	Temperature degrees C
Berkefeld	Potassium Chloride	$1.5 \times 10^{-1}$ normal	Medium	30
		$1.5 \times 10^{-2}$ normal	Large	30
		$1.5 \times 10^{-3}$ normal	Medium	30
		$1.5 \times 10^{-4}$ normal	Medium	30
		$1.5 \times 10^{-5}$ normal	Large	30
Berkefeld	Sodium Chloride	$2 \times 10^{-1}$ normal	Medium	32
		$2 \times 10^{-2}$ normal	Large	32
		$2 \times 10^{-3}$ normal	Large	32
		$2 \times 10^{-4}$ normal	Medium	32
		$2 \times 10^{-5}$ normal	Medium	32
		$2 \times 10^{-6}$ normal	Medium	32
Berkefeld	Lithium Chloride	$2.4 \times 10^{-1}$ normal	Small	30
		$2.4 \times 10^{-2}$ normal	Medium	30
		$2.4 \times 10^{-3}$ normal	Medium	30
		$2.4 \times 10^{-4}$ normal	Medium	30
		$2.4 \times 10^{-5}$ normal	Medium	30
		$2.4 \times 10^{-6}$ normal	Large	30
		$2.4 \times 10^{-7}$ normal	Medium	30
Berkefeld	Barium Chloride	$9 \times 10^{-2}$ normal	Small	30
		$9 \times 10^{-3}$ normal	Medium	30
		$9 \times 10^{-4}$ normal	Medium	30
		$9 \times 10^{-5}$ normal	Large	30
		$9 \times 10^{-6}$ normal	Medium	30
		$9 \times 10^{-7}$ normal	Medium	30
		$9 \times 10^{-8}$ normal	Medium	30
		$9 \times 10^{-9}$ normal	Medium	30
		$9 \times 10^{-10}$ normal	Medium	30
		$9 \times 10^{-11}$ normal	Medium	30
Berkefeld	Aluminum Chloride	$2 \times 10^{-4}$ normal	Medium	29
		$2 \times 10^{-5}$ normal	Large	29
		$2 \times 10^{-6}$ normal	Large	29
		$2 \times 10^{-7}$ normal	Medium	29
		$2 \times 10^{-8}$ normal	Small	29
		$2 \times 10^{-9}$ normal	Medium	29
		$2 \times 10^{-10}$ normal	Large	29
Berkefeld	Thorium Nitrate	$8 \times 10^{-6}$ normal	Medium	30
		$8 \times 10^{-7}$ normal	Medium	30
		$8 \times 10^{-8}$ normal	Large	30
		$8 \times 10^{-9}$ normal	Medium	30
		$8 \times 10^{-10}$ normal	Medium	30
		$8 \times 10^{-11}$ normal	Medium	30
		$8 \times 10^{-12}$ normal	Large	30

The values found for aluminum chloride and thorium nitrate are in good agreement with the concentration of reversal stated by McTaggart. The size of the bubbles in electrolytes depends on the viscosity of the liquid and on the charge of the bubble. At the least addition of electrolyte the negative bubble charge is

TABLE 15 CONCENTRATIONS AT WHICH LARGEST BUBBLES OCCUR

Electrolyte	Concentration
Thorium Nitrate	$10^{-7}$ normal
Aluminum Chloride	$10^{-5}$ normal
Sulfuric Acid	$10^{-5}$ normal
Barium Chloride	$10^{-4}$ normal
Potassium Chloride	$10^{-2}$ normal
Sodium Chloride	$10^{-2}$ normal

decreased and the viscosity increased to an extent which can be observed in the diminution of the size of the bubbles. Upon further addition of electrolyte, the charge of the bubble is reduced to zero. The concentration of reversal is reached. Here the size of the bubble reaches its maximum. However, observation of the size of the bubbles only permits determination of the concentration of reversal for such electrolytes whose viscosity in this dilution does not noticeably exceed that of water. Lithium chloride, whose viscosity is greater according to Arrhenius' data (14) and the foregoing observations, is an example of an electrolyte whose concentration of reversal cannot be determined in this manner.

#### APPLICATIONS

1. Experiments (8) to determine the pore diameters of ceramic filters by blowing air through them, using various liquids for the purpose of measurement, have shown results which scattered over a range of 100 per cent. The effect of viscosity on the production of macroscopically observed gas bubbles or droplets of liquid were indicated at that time. According to the foregoing observations, if this interpretation of the scattering is correct, a filter candle with water measured at the room temperature and with isobutyl alcohol at 80 degrees C would have to give the same value. This experiment was performed on a Berkefeld filter.

	Interface Water/Air at 25 degrees C	Interface Isobutyl- Alcohol/Air at 25 degrees C	Interface Isobutyl- Alcohol/Air at 80 degrees C
Pressure in cm Hg	47	16.5	13
Pore diameter in $\mu$	4.7	4.0	4.6*

\* To calculate this value, the coefficient of temperature of the surface tension is assumed as 2 per cent per degree C. Hence, for isobutyl alcohol/air  $\sigma_{80^{\circ}C} = 20$  dyne/cm.

2. Kautsky and Thiele's (4) experiment stresses that to attain good gas absorption in liquids, liquids of such viscosity should be chosen that the gas bubbles effervesce like fine vapor, thus producing the maximum surface area.

3. It is possible to accelerate flotation by increasing the surface of the gas to a maximum by choosing a suitable viscosity.

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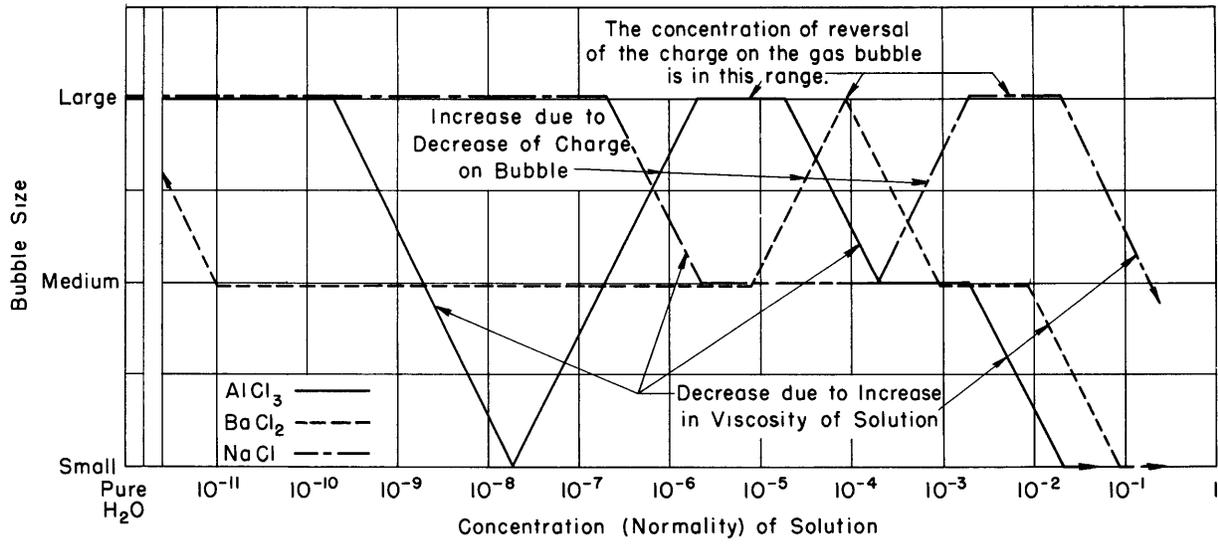
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APPENDIX 1



Typical Curve of Bubble Size as a Function of Concentration (Normality) of Solution

This curve was plotted at the David W. Taylor Model Basin from data given in Table 14 of this translation.

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