The Origin of the Electrical Charge on Small Particles in Water.

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Introduction.

The surface of an air bubble is a particularly simple one at which to examine the electrical conditions which attend all small particles when immersed in a liquid. An air bubble may be considered as a type of coarse suspensoid, which, on being immersed in water, acquires a charge and moves in an electric field as if negatively electrified.

The present work is a continuation of that already published ('Roy. Soc. Proc.,' A, vol. 106, p. 315 (1924)) and deals chiefly with the charge on the bubble immediately after it enters the liquid; this is examined experimentally and also theoretically. In addition, a new method of calculating the potential difference between the bubble surface and the interior of the liquid is suggested.

For convenience, a few results of the former work must first be mentioned. It was there shown that the gas phase has little or no influence on the surface electrification, so that all the electrical effects may safely be ascribed to the surrounding liquid medium. Experimental evidence indicated that the surface phenomena are due to the selective absorption of ions from the water. Furthermore, the mobility of the bubble diminished steadily with increasing purity of the surrounding water. It therefore appears probable that in perfectly pure water the charge would be very small, or even zero.

Experimental.

The experimental arrangements were as described in the former work. A small gas bubble (2 mm. in diameter) is introduced into partially air-free water contained in a cylindrical glass vessel which rotates about a horizontal axis. The bubble then takes up a position on the axis and moves along the latter when an electric field is applied between the two ends of the cell. The mobility is measured continuously as the bubble is slowly absorbed into the water until it finally disappears. After each reading of the velocity, the total time since the introduction of the bubble into the water is also noted, so that the variation of the electrical conditions with the age of the surface can be investigated. It has previously been shown that in water of specific conductivity 1×10^{-6} ohms to 2×10^{-6} ohms^{-1} there is a slow and steady "charging up" of the surface, and that for some time after the introduction of the bubble the charge varies continuously until its final equilibrium state is attained. Since the first object of the present work is a complete investigation of this charging up, water of the above-mentioned purity was used.

For comparison, the experiments were repeated in water of specific conductivity 6×10^{-6} ohms^{-1}; in this water the charging-up period is very short and the velocity of the bubble increases steadily with decreasing radius until the latter is about 0·05–0·1 mm. At about this point the velocity is a maximum and thereafter decreases steadily until the bubble disappears. The explanation of the maximum is not clear. It may represent a true change in the electrification of the surface, or it may be due to increased resistance to the motion of the bubble along the axis. At about this size (0·05 mm. diameter) the bubble ceases to be perfectly stable, and if accidentally disturbed it oscillates about the axis before returning to its equilibrium position. This vibration may increase the resistance of the water to the motion and consequently decrease the mobility. As this point cannot be definitely settled, only bubbles having diameters greater than this minimum will be considered in what follows.

Further experiments were also performed to investigate quantitatively the relation between the charge on the surface and the rate of absorption of the bubble. Air-saturated conductivity water was used after a very small quantity of air had been removed from it by evacuation. A bubble introduced into such water was therefore absorbed very slowly. On completion of this experiment more air was removed from the water and a second bubble introduced. This was absorbed more rapidly than the previous one and gave different results. The process was repeated for a series of bubbles until the rate of absorption became so great as to render further observations impracticable.

If now the bubble is assumed to acquire a definite charge, E, by ionic adsorption, then this charge may be calculated by an application of Stokes' Law. If X is the intensity of the electric field producing the velocity v, η the coefficient of viscosity of water, and r the radius of the bubble, then

$$\mathrm{XE} = 6\pi\eta r v$$

$$\text{or} \quad \mathrm{E} = 6\pi\eta r v/\mathrm{X}.$$

Thus E may be determined directly from a knowledge of v.

The experimental results were represented graphically by plotting the total charge, as calculated above, against either the bubble radius or the age of the surface. The total charge at any time t will indicate very directly the state of adsorption at that time.

Fig. 1 shows a graph of charge against age of surface and was obtained in very pure, air-saturated water. In this water the size of the bubble changes only very slightly during the experiment. It will be observed that the charge is extremely small at first, increases to a maximum, and then falls to a value of about one-third of this maximum. After this stage, the charge on the bubble surface appears to be independent of the time.

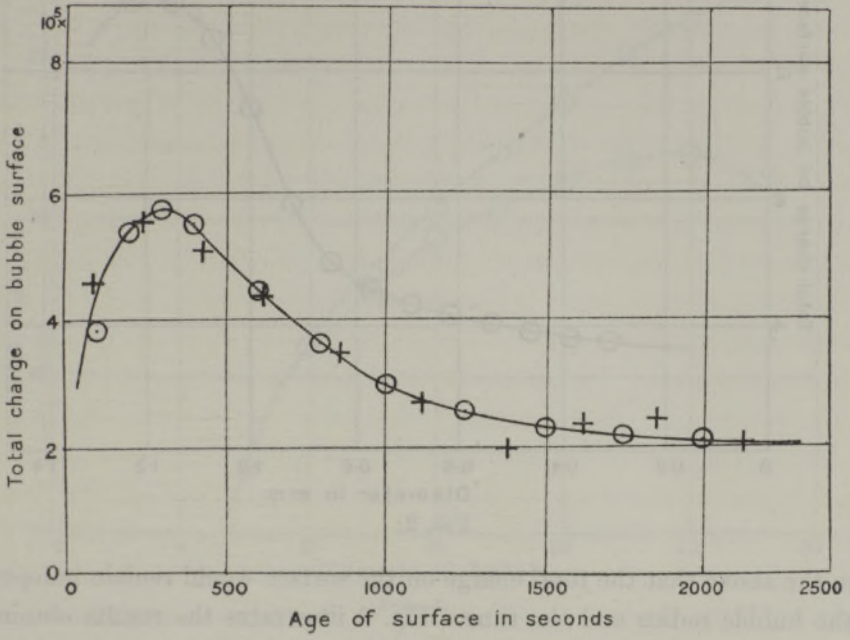

Fig. 1.

These experiments were repeated in water from which some air had been removed so that the diameter of the bubble decreased continuously during the experiment. It was found that the curve obtained was very similar to that in fig. 1, and that when equilibrium had been attained the total charge on the bubble remained independent not only of time but also of bubble diameter. This is somewhat surprising and appears to indicate that, once an equilibrium state is reached, the surface density of charge must increase inversely as the square of the bubble radius, since the total charge remains practically constant while the bubble area shrinks, sometimes down to about 1/20 of its original size. Fig. 2 illustrates one of these experiments.

The experiments in water of higher specific conductivity test this point further. In this water the charging-up period is very short so that after the first few readings the equilibrium state is reached, and it might then be expected from the above that the total charge on the surface would remain independent of the bubble radius and the time. Fig. 3 illustrates the results obtained in such water. For the whole range of diameters the total charge remains almost constant, decreasing very slightly with decreasing radius.

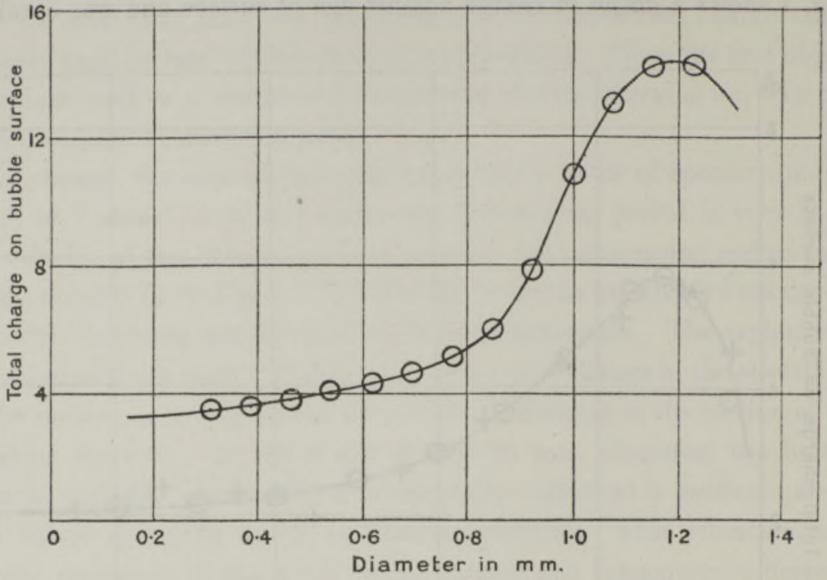

FIG. 2.

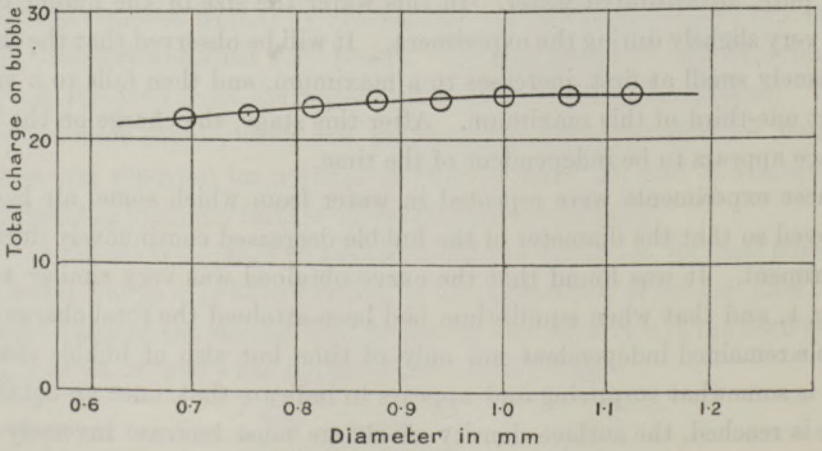

FIG. 3.

It was found possible to obtain the above type of graph (fig. 3) only when the rate of absorption of the bubble was very slow. If the rate of absorption were great the total charge decreased steadily from the first observation.

Fig. 4 shows the results obtained from two successive experiments in which the water used had the same conductivity but contained a different amount of air in each experiment. An examination of such curves shows that the greater the rate of absorption the greater the initial equilibrium charge. (Fig. 3 and fig. 4 together indicate that for zero rate of absorption the total charge is independent of the radius of the bubble.) It will later be shown that there is a quantitative relation between the rate of absorption of the bubble and its charge. This is illustrated in fig. 5.

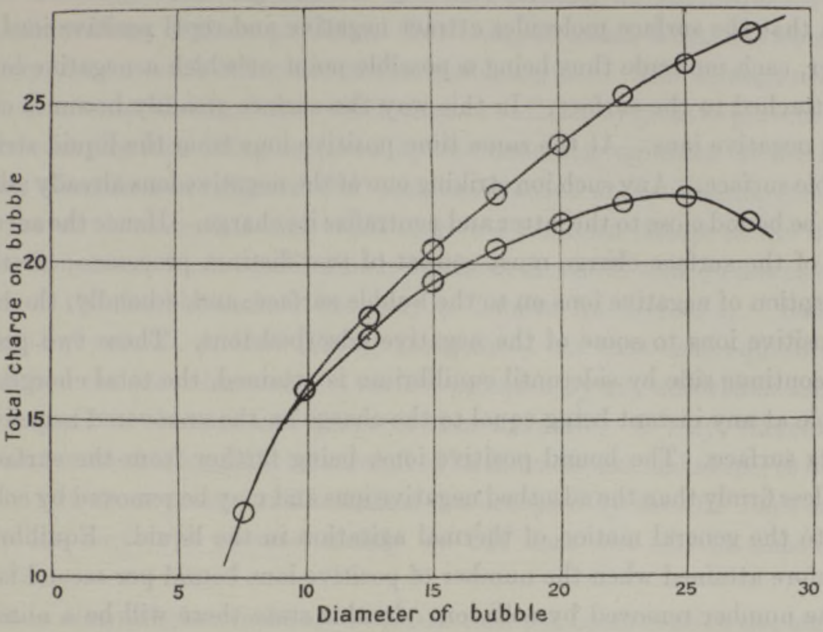

FIG. 4.

In all experiments the velocity of the bubble was measured using two different values of the electric field (X) alternately. In this way the velocity was shown to be proportional to the applied field throughout the charging period as well as through the subsequent history of the bubble.

Theoretical.

The results previously obtained as well as those described above conflict with the usual theories as to the electrical structure of the surface of small particles in water. This being so, an endeavour is made here to account for the whole phenomenon on the basis of adsorption, and the relations deduced are compared with experiment.

When a bubble is first introduced into water, the surface is composed of water molecules, which being polar are all orientated and thus have a resultant electric field. Since the bubble acquires a negative charge, this orientation must be such that the surface molecules attract negative and repel positive ions in the water, each molecule thus being a possible point at which a negative ion may be attached to the surface. In this way the surface steadily becomes covered with negative ions. At the same time positive ions from the liquid strike the bubble surface. Any such ion striking one of the negative ions already adsorbed may be bound close to the latter and neutralise its charge. Hence the accumulation of the surface charge must consist of two distinct processes; firstly, the adsorption of negative ions on to the bubble surface, and, secondly, the binding of positive ions to some of the negative adsorbed ions. These two processes will continue side by side until equilibrium is attained, the total charge on the bubble at any instant being equal to the charge on the uncovered negative ions on its surface. The bound positive ions, being farther from the surface, are held less firmly than the adsorbed negative ions and may be removed by collisions due to the general motion of thermal agitation in the liquid. Equilibrium is therefore attained when the number of positive ions bound per second is equal to the number removed by collision. In this state there will be a number of uncovered negative ions as well as a number covered. In this connection it is of interest to note that Rinde ('Phil. Mag.,' vol. 1, p. 32 (January, 1926)) found that on sulphur particles in an acid solution both Cl' ions and also neutral HCl molecules were adsorbed. The process of adsorption in this case may be very similar to that under discussion, the neutral molecules being due to the covering of the Cl' ions.

In these experiments pure distilled water was used so that the ions present would be chiefly H^+ and OH'. In addition, there would be minute traces of electrolytic impurities from the glass of the cell, etc., giving rise to ions which for convenience may be called X' and Y^+. These in comparison with the hydrolytic ions must be extremely few in number, and this number must decrease with increasing purity of the water. On the other hand, the hydrolytic ions are still present in relatively large numbers even in water of the greatest purity, the ionisation of pure water yielding about 10^{13} H^+ and OH' ions per c.c. Consequently it is impossible by purification to remove all ions from the water. Nevertheless, it was found that the greater the purity of the water (as measured by its electrical conductivity) the lower the mobility of the bubble, which in some cases was reduced as low as 1 per cent. of its normal value. From these considerations it is evident that the charge on the bubble is *not* produced by the H^+ and OH' ions, but is due almost entirely to the presence of stray ions X' and Y^+ in the water.

The inactivity of the H^+ and OH' ions may possibly be a consequence of the small dimensions of these particles. For being so small, when adsorbed they are very close to each other and to the bubble surface. This arrangement will result in intense binding forces which may be sufficiently great to prevent many of the covering ions being removed by the molecular agitation of the liquid. Hence, when the adsorption of OH' ions has reached an equilibrium condition, very few of them are left uncovered to give a resultant charge to the bubble. At the same time, when equilibrium is attained, these OH' ions do not cover the whole of the bubble surface but only a definite fraction of it. Langmuir ('J.A.C.S.,' vol. 40, p. 1367 (1918)) has pointed out that once equilibrium is established the exact fraction of a surface occupied by any adsorbable molecule may depend on the size and shape of that molecule. It may, therefore, be possible for another ion (X'), on account of its different size and shape, to become attached to those points on the surface not occupied by the OH' ions, so that finally the surface is covered mainly by OH' ions but also to some extent by X' ions.

If it is assumed that there are 10^{13} OH' ions per cubic centimetre, and that any one of them striking an unoccupied surface molecule remains attached, then a simple calculation indicates that these ions cover 90 per cent. of the surface in about 1/100 sec. Since the adsorption of covering H^+ ions proceeds concurrently, only a very brief interval of time is required for the adsorption of both these ions to reach its equilibrium state, and this even in the purest water.

The adsorption of X' ions will be a much slower process owing to their scarcity. In exactly the same way as for H^+ and OH' ions, the adsorbed X' ions will be covered in their turn by Y^+ ions from the liquid. Since X' and Y^+ are larger than OH' and H^+, they will be unable to approach so closely to each other and the binding forces will therefore be weaker. For this reason the Y^+ ions will be more readily removed by the thermal agitation of the surrounding liquid. Hence a certain fraction of the adsorbed X' ions when in equilibrium will still be uncovered, and it is to *these* that the bubble owes its charge. In the very pure water the number of such stray ions as X' and Y^+ is small and as a result the equilibrium state is attained but slowly.

According to this view the H^+ and OH' ions, although so numerous and occupying a large fraction of the surface, add but little to the bubble charge owing to the tight binding existing between them. Their chief function then appears to be that of limiting the number of possible points at which other ions can be adsorbed.

Since such ions as X′ and Y^+ occur simply as impurities in the water and always in very minute concentrations, their exact number would be expected to vary from one experiment to another even when the specific conductivity remains practically constant. For this reason the rate at which the bubble acquires its charge in the purest water may vary widely in the different experiments. Such variation is found in practice, the longest charging period being shown in fig. 1. In other experiments in water of the same conductivity, the period varied from this value to 100 secs. These variations are observed only in the purest water.

Although the number of X′ and Y^+ ions present varies in this way, they are always so scarce that the conductivity of the pure water is chiefly due to the ions H^+ and OH′. Thus the fact that the rate of charging varies while the conductivity remains practically constant (1×10^{-6} ohms^{-1}) is in accordance with the view that the charge is due to stray ions X′ and Y^+ and not to the hydrolytic ions.

The experiments described show that in equilibrium the number of uncovered ions per square centimetre of surface is inversely proportional to the square of the radius. This relation would hold true if the numbers (N_x) of negative ions and (N_y) of positive ions per square centimetre each varied inversely as the square of the radius. N_x and N_y also depend on the age of the bubble surface so that it may be assumed that

$$\left.\begin{aligned} N_x &= \frac{f(t)}{r^2} \\ N_y &= \frac{g(t)}{r^2} \end{aligned}\right\}, \tag{1}$$

where $f(t)$ and $g(t)$ are functions of t.

Hence the total charge on the bubble $= 4\pi r^2 . (N_x - N_y) = 4\pi \{f(t) - g(t)\}$, which is independent of r, in accordance with experiment.

Making certain assumptions it is now possible to calculate the total charge on the bubble at any time t after its formation. For convenience, these assumptions are tabulated as follows :—

1. A fraction α of the bubble surface is alone capable of adsorbing the X′ ions from the water. The remaining fraction $(1 - \alpha)$ is occupied by H^+ and OH′ ions in loose combination. These prevent the close approach and adsorption of X′ ions to the surface.
2. Each adsorbed X′ ion is attached to a single surface water molecule.

3. The forces between an X′ ion and the surface molecule to which it is attached are great enough to prevent appreciable re-evaporation of the X′ ions. Hence any such ion striking an unoccupied surface molecule remains attached.
   (Evidence of this assumption is given later, p. 246.)

Let there be n_x of the X′ ions per c.c. of the liquid.
,, v_x be their average velocity of thermal agitation (velocity of mean square).
,, γ be the surface area occupied by one adsorbed X′ ion = area of a surface water molecule.
,, α be the fraction of the surface occupied in equilibrium by X′ ions.

α then depends on the radius of the bubble and $= \beta/r^2$ (experimental). Let $N_x =$ number of X′ ions adsorbed per unit area at time t. Then the number striking unit area per unit time is $n_x v_x/\sqrt{6\pi}$.

Fraction of the area occupied by OH′ ions $= (1 - \alpha)$.

Fraction of the area occupied by X′ ions at time $t = \gamma N_x$.

Therefore fraction of the whole surface which is unoccupied at time $t = \alpha - \gamma N_x$ and the number of free X′ ions striking these unoccupied spaces per second

$$= \frac{n_x v_x}{\sqrt{6\pi}} (\alpha - \gamma N_x).$$

If all collisions between surface molecules and free X′ ions result in adsorption and if re-evaporation is negligible, then

$$\frac{dN_x}{dt} = \frac{n_x v_x}{\sqrt{6\pi}} (\alpha - \gamma N_x).$$

The solution of this is

$$N_x = \frac{\alpha}{\gamma}\left(1 + Ce^{-\frac{n_x v_x \gamma}{\sqrt{6\pi}}t}\right).$$

But $N_x = 0$ when $t = 0$. Therefore

$$N_x = \frac{\alpha}{\gamma}\left(1 - e^{-\frac{n_x v_x \gamma}{\sqrt{6\pi}}t}\right) \qquad (2)$$

= number of adsorbed X′ ions at time t.

Let the same symbols as above, with suffix y, refer to the Y^+ ions. Since these ions are bound to the surface only when they strike an adsorbed X′ ion, the chance of any Y^+ ion becoming bound is proportional to the fraction of the surface occupied by uncovered X′ ions.

Fraction of surface occupied by uncovered X′ ions $= \gamma (N_x - N_y)$.

Therefore the increase in the number of Y^+ ions attached to unit area of the surface in time dt

$$= \frac{n_y v_y}{\sqrt{6\pi}} (N_x - N_y) \gamma \, dt.$$

At the same time, some of those already attached are removed by the thermal agitation of the liquid.

Let k = fraction of the positive covering ions removed per second in this manner. Then the equation for N_y is

$$\frac{dN_y}{dt} = \frac{n_y v_y \gamma}{\sqrt{6\pi}} (N_x - N_y) - kN_y, \tag{3}$$

when

$$t = \infty, \quad \frac{dN_y}{dt} = 0 \quad \text{and} \quad N_x = \alpha/\gamma.$$

Therefore

$$N_y = \frac{\alpha/\gamma}{1 + \frac{\sqrt{6\pi}\, k.}{n_y v_y \gamma}} \tag{4}$$

The number of uncovered negative ions in equilibrium is therefore $(N_x - N_y)$ per square centimetre,

$$= \frac{\alpha}{\gamma} \left\{ 1 - \frac{1}{1 + \frac{\sqrt{6\pi} \,.\, k}{n_y v_y \gamma}} \right\} = \frac{k\alpha}{\gamma} \left\{ \frac{1}{k + \frac{n_y v_y \gamma}{\sqrt{6\pi}}} \right\} \tag{5}$$

= surface density on the bubble when equilibrium is attained.

Returning to equation (3)

$$\frac{dN_y}{dt} + N_y \left(\frac{n_y v_y \gamma}{\sqrt{6\pi}} + k \right) = \frac{n_y v_y \gamma}{\sqrt{6\pi}} N_x.$$

$$= \frac{n_y v_y \gamma}{\sqrt{6\pi}} \cdot \frac{\alpha}{\gamma} \cdot \left(1 - e^{-\frac{n_x v_x \gamma}{\sqrt{6\pi}} t} \right) \qquad \text{by equation (2)}$$

Hence

$$N_y = n_y v_y \alpha \left[\frac{1}{n_y v_y \gamma + \sqrt{6\pi} k} - \frac{e^{-\frac{n_x v_x \gamma}{\sqrt{6\pi}} t}}{(n_y v_y \gamma - n_x v_x \gamma + \sqrt{6\pi} k)} \right.$$

$$\left. + \frac{n_x v_x \gamma e^{-\left(\frac{n_y v_y \gamma}{\sqrt{6\pi}} + k\right) t}}{(n_y v_y \gamma + \sqrt{6\pi} k)(n_y v_y \gamma - n_x v_x \gamma + \sqrt{6\pi} k)} \right].$$

Also

$$N_x = \frac{\alpha}{\gamma} \left(1 - e^{-\frac{n_x v_x \gamma}{\sqrt{6\pi}} t} \right).$$

But the number of uncovered negative ions per square centimetre $= (N_x - N_y)$. Therefore $M =$ total number of uncovered negative ions on surface of bubble $= 4\pi r^2 (N_x - N_y)$

$$= \frac{4\pi\beta}{\gamma}\left[\frac{k}{\frac{n_y v_y \gamma}{\sqrt{6\pi}} + k} + \frac{n_x v_x - \sqrt{6\pi}\,\frac{k}{\gamma}}{n_y v_y - n_x v_x + \sqrt{6\pi}\,\frac{k}{\gamma}}\, e^{-\frac{n_x v_x \gamma}{\sqrt{6\pi}} t} \right.$$

$$\left. - \frac{n_x v_x n_y v_y e^{-\left(\frac{n_y v_y \gamma}{\sqrt{6\pi}} + k\right) t}}{\left(n_y v_y + \sqrt{6\pi}\,\frac{k}{\gamma}\right)\left(n_y v_y - n_x v_x + \sqrt{6\pi}\,\frac{k}{\gamma}\right)}\right]. \qquad (6)$$

This expression (6) then gives the number of free negative ions on the bubble surface at time t. If the ions X' and Y^+ are monovalent then the charge on the bubble at time t is $M.\varepsilon$., e.s.u. ($\varepsilon =$ ionic charge).

The constants β and k are evaluated below. Using the values there obtained, equation (6) reduces to

$$M = 1{\cdot}91 \times 10^6 [0{\cdot}1096 + 1{\cdot}19\, e^{-3\cdot 23 \times 10^{-3} t} - 1{\cdot}299\, e^{-5\cdot 44 \times 10^{-3} t}]. \qquad (7)$$

The values of the total charge as calculated from (7) are shown in fig. 1 by points marked ⊙. The points + are experimental values. It will be seen that the agreement is exceedingly good. This agreement between theory and experiment lends support to the present view of surface electrification.

Evaluation of β and k.

The constants β and k used in the above expression furnish much information regarding the number of negative and positive ions on the surface at any time. From the measurement of the electric charge at any instant only the *difference* between the number of negative and positive adsorbed ions is obtained. By definition of β the total number of adsorbed negative ions on the bubble when equilibrium is attained is given by

$$4\pi r^2 \frac{\alpha}{\gamma} = \frac{4\pi\beta}{\gamma},$$

and therefore can be obtained directly from a knowledge of β.

In order to evaluate β the above expression for M (equation 6) is applied to the experimental curves. Considering a representative graph (fig. 1), the total charge on the bubble attained a maximum value after 300 seconds, this value being $5{\cdot}66 \times 10^5\ \varepsilon$. Hence if the adsorbed ions were monovalent, the number of uncovered negatives at this instant was $5 \cdot 66 \times 10^5$. Finally when equilibrium conditions obtained on the surface the total charge was $2 \cdot 093 \times 10^5\ \varepsilon$. Hence the experimental conditions may be expressed.

$$\left.\begin{array}{ll} t = 300 \text{ secs.}\ \dfrac{d\mathrm{M}}{dt} = 0 & \mathrm{M} = 5 \cdot 66 \times 10^5 \\ t = \infty & \mathrm{M} = 2 \cdot 093 \times 10^5. \end{array}\right\} \qquad (8)$$

In equation (5) there occurs the average velocities of thermal agitation v_x and v_y of the two ions. These are not known accurately owing to the uncertainty of the nature of the ions X′ and Y⁺, but, since in temperature equilibrium the kinetic energy of a liquid molecule is equal to that of a gaseous molecule, an approximation to the required values may be made from a knowledge of the mean square velocities of gaseous molecules. These range in general from 1×10^4 cm./sec. to 5×10^4 cm./sec., so that the desired values must lie in this region. For the purposes of calculation, therefore, it may be assumed that

$$v_x = 2 \times 10^4 \text{ cm./sec.}$$
$$v_y = 3 \times 10^4 \text{ cm./sec.}$$

This assumption, while being only approximately correct, will alter only the numerical value of the constants obtained from equation (6); it cannot affect their order of magnitude, which is of primary interest. It will be shown later that any error here introduced is negligible in the calculation of the potential difference at the surface. On differentiating (6), inserting the above conditions (8) and putting $n_x = n_y = n$, the constants are found to have values

$$n = 7 \times 10^8.$$
$$k = 5 \cdot 96 \times 10^4.$$
$$\beta = 1 \cdot 5 \times 10^{-10}.$$

This shows that the ions X′ and Y⁺, due to chance electrolytic impurity, are very few in number compared with the H⁺ and OH′ ions.

The constant k gives very useful information as to the binding of the covering Y⁺ ions. It appears that only about 6×10^{-4} of these ions are removed per second by impact with surrounding molecules. These positive ions are farthest from the water surface and will therefore be least firmly bound to it. Hence, in the case of the *negative* ions, which are even more firmly bound, the number removed per second is quite negligible, and the assumption that all the negative ions striking blank spaces remain attached would seem to be justified.

The total number of negative ions on the surface when equilibrium is attained is

$$4\pi\beta/\gamma = 1 \cdot 85 \times 10^6.$$

The number of *uncovered* negative ions, as measured by the resultant charge on the bubble is $2 \cdot 09 \times 10^5$. These figures therefore indicate that about 89 per cent of the adsorbed X′ ions are covered by bound positive ions, while only about 11 per cent. are uncovered and thus charge the surface negatively.

From these figures the constitution of the surface layer of the bubble may be summed as follows :—

Taking the number of water molecules per square centimetre as equal to 10^{15}, the very great majority of them are covered by H^+ and OH' ions which are bound so tightly to the surface that very few of them "evaporate" to give a resultant charge. There are also $2 \cdot 35 \times 10^8$ negative ions of larger size attached per square centimetre and of these 89 per cent. are covered by positive ions which are continually evaporating and recondensing on the negatives, the fraction evaporating per second being $6 \cdot 0 \times 10^{-4}$. In this way a definite resultant charge is given to the bubble by those negative ions which are momentarily uncovered.

Relation between the Charge and the Rate of Absorption of the Bubble.

The above adsorption hypothesis is further confirmed by an examination of the bubble charge after the surface is fully formed. At this stage the adsorption has reached a state of dynamic equilibrium. Hence, from equations (2) and (3), when $t = \infty$, $\frac{dN_y}{dt} = 0$,

$$\therefore \quad N_x = \alpha/\gamma, \qquad \frac{n_y v_y \gamma}{\sqrt{6\pi}}(N_x - N_y) = kN_y.$$

Therefore

$$N_y = \frac{\alpha/\gamma}{1 + \frac{k\sqrt{6\pi}}{n_y v_y \gamma}}.$$

The equilibrium charge is therefore

$$4\pi r^2 (N_x - N_y) = \frac{4\pi\beta}{\gamma}\left(1 - \frac{1}{1 + \frac{k\sqrt{6\pi}}{n_y v_y \gamma}}\right)$$

$$= \frac{4\pi\beta/\gamma}{1 + \frac{n_y v_y \gamma}{k\sqrt{6\pi}}}. \qquad (9)$$

This is the equilibrium charge when the bubble is *not* being absorbed into the water. But when air-free water is used, the gas molecules pass through the surface in a continuous stream. Consequently more positive ions will be removed by collisions between them and the incoming air molecules. Hence the total charge on the bubble is greater the faster the bubble is absorbed.

The number of positive covering ions removed by the air molecules will obviously be proportional to the number of air molecules passing per second through unit area of the surface, and also to the number of positive ions present per sq. cm. of surface. But the rate of absorption of the bubble is

$$\frac{d(\text{Vol.})}{dt} = 4\pi r^2 \frac{dr}{dt}.$$

Therefore the number of air molecules passing through one square centimetre per second is dr/dt. Then the equation giving the number of positive ions per square centimetre will become

$$\frac{d\mathrm{N}_y}{dt} = \frac{n_y v_y \Upsilon}{\sqrt{6\pi}}(\mathrm{N}_x - \mathrm{N}_y) - k\mathrm{N}_y - \mathrm{C}\mathrm{N}_y \frac{dr}{dt}$$

where C is a constant.

In equilibrium

$$\frac{d\mathrm{N}_y}{dt} = 0 \quad \text{and} \quad \mathrm{N}_x = \frac{\alpha}{\Upsilon}.$$

Therefore

$$\mathrm{N}_y = \frac{\alpha/\Upsilon}{1 + \dfrac{\left(k + \mathrm{C}\dfrac{dr}{dt}\right)\sqrt{6\pi}}{n_y v_y \Upsilon}},$$

and the charge per unit area

$$= \mathrm{N}_x - \mathrm{N}_y = \frac{\alpha}{\Upsilon}\left\{1 - \frac{1}{1 + \dfrac{\left(k + \mathrm{C}\dfrac{dr}{dt}\right)\sqrt{6\pi}}{n_y v_y \Upsilon}}\right\}$$

$$= \frac{\alpha}{\Upsilon}\left\{\frac{1}{1 + \dfrac{n_y v_y \Upsilon}{\left(k + \mathrm{C}\dfrac{dr}{dt}\right)\sqrt{6\pi}}}\right\}.$$

The total charge is

$$\frac{4\pi\beta}{\Upsilon}\left\{\frac{1}{1 + \dfrac{n_y v_y \Upsilon}{\left(k + \mathrm{C}\dfrac{dr}{dt}\right)\sqrt{6\pi}}}\right\} = \mathrm{M}, \tag{10}$$

but

$$\mathrm{M}_0 = \frac{4\pi\beta}{\Upsilon}\left\{\frac{1}{1 + \dfrac{n_y v_y \Upsilon}{k\sqrt{6\pi}}}\right\}$$

= total charge when rate of absorption is zero.

Therefore

$$M - M_0 = \frac{(96\pi^3)^{\frac{1}{2}} n_y v_y \beta C \dfrac{dr}{dt}}{\left\{\left(k + C\dfrac{dr}{dt}\right)\sqrt{6\pi} + n_y v_y \gamma\right\}\left\{k\sqrt{6\pi} + n_y v_y \gamma\right\}}$$

and

$$\frac{1}{M - M_0} = \frac{(k\sqrt{6\pi} + n_y v_y \gamma)}{4\pi n_y v_y \beta} + \frac{(k\sqrt{6\pi} + n_y v_y \gamma)^2}{(96\pi^3)^{\frac{1}{2}} n_y v_y \beta C}\,\frac{dt}{dr}$$

$$= \left(\frac{k\sqrt{6\pi} + n_y v_y \gamma}{4\pi n_y v_y \beta}\right)\left(1 + \frac{k\sqrt{6\pi} + n_y v_y \gamma}{\sqrt{6\pi} C}\,\frac{dt}{dr}\right)$$

or

$$\frac{1}{M - M_0} = A + B\,\frac{dt}{dr},$$

where A and B are constants so long as n, v and k are constant.

If now a series of bubbles of constant diameter are examined in water of constant conductivity but containing different quantities of air in solution,

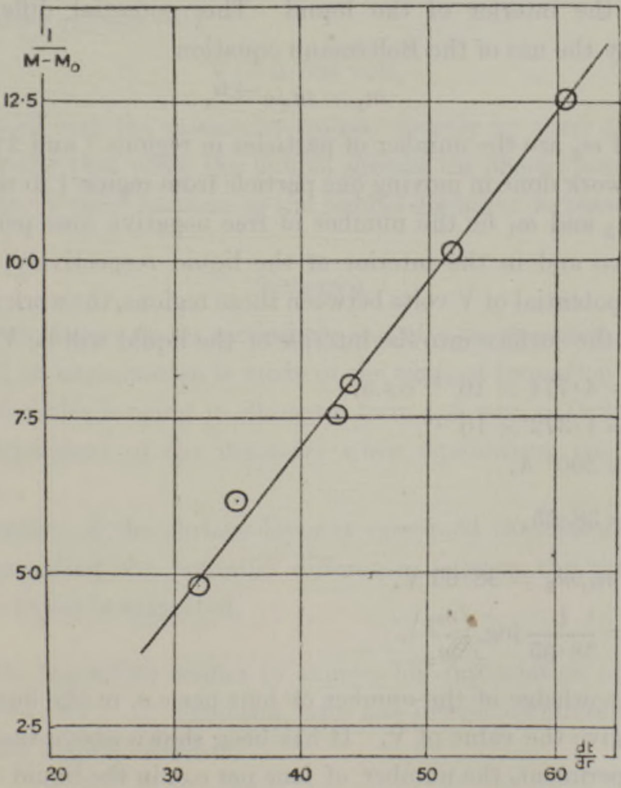

Fig. 5.

then n, v and k will be constant and by the above equation there should be a straight line relation between $1/(\mathrm{M} - \mathrm{M}_0)$ and dt/dr.

This has been examined experimentally. A bubble of 0·05 cm. diameter was used in air-saturated water. The equilibrium charge on this bubble gives the value of M_0. The charge (M) on a bubble of the same diameter was then measured in a series of experiments in water unsaturated by air. By using water of various degrees of air saturation values of M could be determined for various values of dr/dt (measured experimentally). The $1/(\mathrm{M} - \mathrm{M}_0)$ was then calculated and plotted against dt/dr. The result is seen in fig. 5, which is a straight line graph and offers strong evidence in support of the theory.

Evaluation of the Potential Difference between the Surface and the Interior of the Liquid.

Since it is assumed that an air bubble has a resultant charge, Helmholtz' equation may not be applied. On the other hand, the concentration of adsorbed ions on the bubble surface will result in a potential difference between the surface and the interior of the liquid. This potential difference may be determined by the use of the Boltzmann equation

$$m_1 = m_2\, e^{-\psi/kt},$$

where m_1 and m_2 are the number of particles in regions 1 and 2 in equilibrium, and ψ is the work done in moving one particle from region 1 to region 2.

Now let m_2 and m_1 be the number of free negative ions per c.c. near the bubble surface and in the interior of the liquid respectively. If there is a difference of potential of V volts between these regions, the work done in moving one ion from the surface into the interior of the liquid will be $\mathrm{V}e/300$ ergs.

Taking $e = 4{\cdot}774 \times 10^{-10}$ e.s.u.

$k = 1{\cdot}372 \times 10^{-16}$.

$\mathrm{T} = 300°$ A.

$$\therefore \frac{e}{k\mathrm{T}} = 38{\cdot}65,$$

$$\therefore \log_e m_1/m_2 = 38{\cdot}65\ \mathrm{V},$$

or

$$\mathrm{V} = \frac{1}{38{\cdot}65} \log_e \left(\frac{m_1}{m_2}\right). \tag{11}$$

Hence a knowledge of the number of ions per c.c. in the liquid and on the surface will give the value of V. It has been shown above that in one representative experiment, the number of ions per c.c. in the liquid was $7{\cdot}0 \times 10^8$. For the evaluation of m_2 it is only necessary to consider the uncovered negative ions on the surface, since those having a positive ion attached will exert no repulsion on another negative ion approaching the surface.

In equilibrium in the above experiment, the number of such ions on the bubble was $2\cdot09 \times 10^5$. Consider the time at which the area of the bubble was 5×10^{-2} square cms.

Then the number of ions attached per square cm. $= 4\cdot18 \times 10^6$ and average distance between these ions $= \left(\frac{1}{4\cdot18 \times 10^6}\right)^{\frac{1}{2}}$

$$= 4\cdot89 \times 10^{-4} \text{ cm.}$$

Hence in a small volume close to the bubble surface the negative ions are $4\cdot89 \times 10^{-4}$ cm. apart. Consequently the number per c.c. in this region is $\left(\frac{1}{4\cdot89 \times 10^{-4}}\right)^3 = 8\cdot55 \times 10^9$,

hence

$$m_1 = 7\cdot0 \times 10^8.,$$

$$m_2 = 8\cdot55 \times 10^9.,$$

and therefore by equation (11)

$$\mathrm{V} = 0\cdot064 \text{ volt},$$

which agrees well with the values determined directly by other observers.

Since it is found that while the bubble shrinks the charge remains constant, m_2 and therefore V must increase as the bubble diameter decreases.

Summary.

The electrical charge on an air bubble in water is measured under various conditions and an examination is made of the mode of formation of this surface charge. For bubbles ranging in diameter from 2·0 mm. to 0·2 mm. the total charge is independent of the diameter when equilibrium conditions obtain at the surface.

The constitution of the surface layer is examined theoretically and a new method of measuring the potential difference between the surface and the interior of the liquid is suggested.

In conclusion the writer wishes to express his appreciation of the unfailing kindness of Prof. Sir J. J. Thomson, who has interested himself in the work and given much helpful criticism.