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10 February 1967

Efflux Time of Soap Bubbles and Liquid Spheres

Abstract. *The efflux time,* T, *of gas from soap bubbles of radius,* R, *through their blow tube of length,* l, *and radius,* ρ, *is given by the equation*

$$T_{start\rightarrow end} = \frac{2\cdot\eta\cdot l}{\sigma\cdot\rho^4}(R^4_{start} - R^4_{end})$$

where η *is the viscosity of the gas and* σ *the surface tension of the bubble solution, all in centimeter-gram-second units. Similar relations between time and diameter were established for the flow from one bubble to another or from one bubble within another. The same relations hold for the flow of liquid spheres, suspended in another liquid of equal density, following Plateau's classic method. They have been extended to the flow of spheres to cylinders and catenoids of rotation. In all these cases the driving force is the surface or interfacial tension, creating an excess pressure as defined by Laplace's equation.*

During my recent experiments on the solidification of soap bubbles (*1*), I could not find any published information on the shrinkage in size of soap bubbles, as the air flows out of them through the blow tube, as a function of time (*1–4*). Likewise Plateau's (*2*) liquid spheres suspended at zero gravity in a nonmiscible liquid, and the flow from one sphere to another, either a soap bubble or a liquid, or from a sphere to a cylinder have not been studied. Furthermore, the change in shape, for example from a cylinder to catenoid of rotation, has not been investigated. Even the much simpler two-dimensional analogon, that is, the flow of the Langmuir liquid lens through a channel into another lens, floating on a nonmiscible liquid, has not been investigated. Yet similar systems, where the flow is determined by surface tension forces, may occur in biological systems [for example, the giant cell with a channel (*5*)].

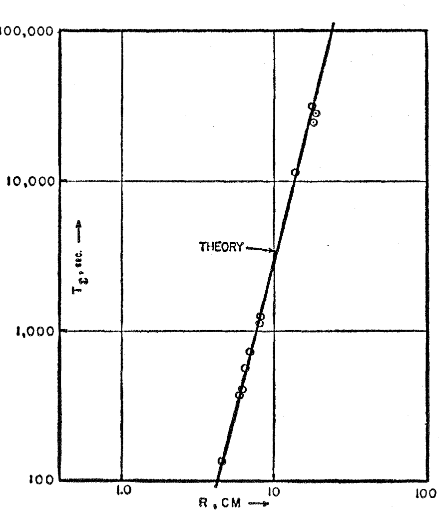

Fig. 1. Experimental efflux time of soap bubbles, in seconds, plotted against their radius, in centimeters.

I measured the efflux time of soap bubbles and other liquid spheres through the blow tube as a function of the diameter of the bubble or sphere. Efflux time is the time necessary for air (or any other gas) to flow out of the bubble as it is pressed out by its surface tension, σ, through the open blow tube of uniform inner radius, ρ, and length, l, as its radius at the start (R_{start}) is diminished to R_{end}, at the instant the tube is closed again. The total efflux time, T_Σ, is the time necessary for the complete disappearance of the bubble, that is, $R_{\text{end}} = 0$.

Soap bubbles were blown from a diameter of a few millimeters to 50 cm from soap solutions (*1, 6*). For protection, they were blown in (i) a rectangular glass fish aquarium, (ii) in a clear Plexiglas cube with a 55.9-cm edge made for me by the Dynalab Corporation of Rochester, New York, and (iii) in a 72-liter pyrex flask manufactured and donated by the Corning Glass Works.

The diameter of bubbles was first measured with two sliding plumb bobs, and later with a cathetometer. The image of small bubbles was magnified and projected onto a screen. Efflux times were measured with a watch or stopwatch in the range of a few seconds to over an hour. Four calibrated flow tubes were used. All results were monitored to a standard tube which has a length, l, of 29.0 cm and an inner radius, ρ, of 0.205 cm (its tube funnel had a tip with an outside radius, ρ_{out}, of 1.93 cm).

The efflux times obtained with the other tubes were multiplied by the ratios of the experimental flow tube constants and all results are shown on a log–log plot in Fig. 1. The experimental results with this standard tube alone are given by the equation:

$$T_\Sigma = 0.27\cdot R^{3.96} \quad (1)$$

The exact theoretical line is given by the expression $T_\Sigma = 0.31\cdot R^4$ (T is in seconds, R in centimeters).

In view of the good agreement, I conclude that the total efflux time is proportional to the fourth power of the radius (or diameter) of the bubble.

The exact law and the interpretation of the constant, c, can be arrived at by simple mathematics. The decrease in volume of a bubble sphere, dV, if its radius, R, is decreased by an amount, dR, is:

$$dV = 4\pi R^2\cdot dR \quad (2)$$

The same volume element of gas, dV, of viscosity, η, flowing through a tube l cm long and with a radius, ρ, in the time, dt, equals, following Poiseuille's law (*7*):

$$dV = \frac{\Delta P\cdot\rho^4\cdot\pi}{8\cdot l\cdot\eta}\cdot dt \quad (3)$$

From these two expressions and since for a soap bubble $\Delta P = 4\sigma/R$, I obtain, after integrating,

$$T_{start\rightarrow end} = \frac{2\cdot\eta\cdot l}{\sigma\cdot\rho^4}(R^4_{start} - R^4_{end}) \quad (4)$$

Therefore $c_{\text{theory}} = 2\cdot\eta\cdot l/\sigma\cdot\rho^4$ and I obtain the value 0.31 sec/cm^4, using 28.6 dyne/cm for σ and 183 μpoise for η (air, 20°C), in close agreement with the experimental value in Eq. 1. It should be remembered that only a 1-percent error in both R and ρ causes an 8-percent error in the con-

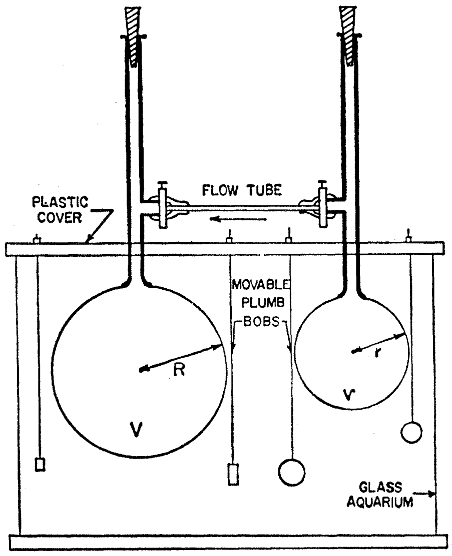

Fig. 2. Two soap bubbles connected by a flow tube in a glass aquarium, for the observation of their efflux time.

stant; an additional error of 1 percent in both σ and η would cause the total error to increase to about 10 percent.

This simple relationship (Eq. 4) can now be used to measure either σ or η. It has been used to investigate surface film properties at low temperatures (*1*).

More precise work in the future should take into account two main factors which affect the accuracy of measurements and any departure from Eq. 4: deviation of the bubble from ideal spherecity, and "dead" areas which do not contract, that is, the area of the blow tube and the liquid drop hanging at the bottom of the bubble.

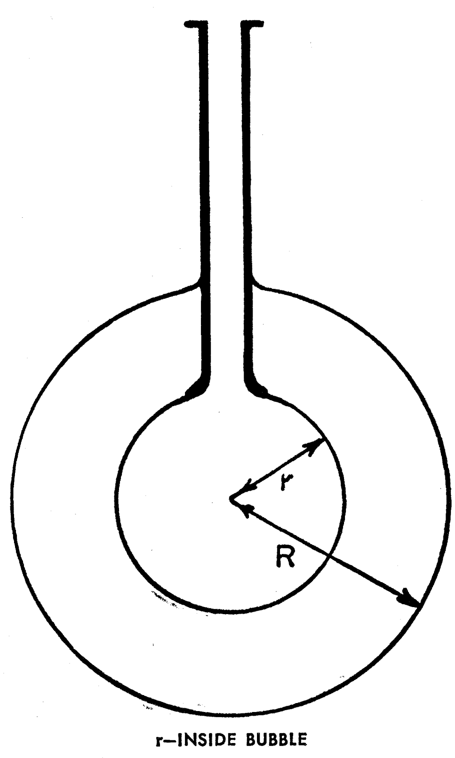

Fig. 3. Double soap bubble hanging on a blow tube.

Plateau (*2*) and Boys (*4*) have shown that if two bubbles of radii R and r are connected by a flow tube as shown in Fig. 2, the larger bubble grows at the expense of the smaller one until the latter disappears into a flat film; the time relationship, however, has not been established.

If, as in Fig. 2, R is slightly larger than r, its internal pressure is slightly smaller than that in the r-bubble. Therefore, air (or gas) is pressed into the larger bubble by the pressure difference:

$$\Delta P = 4\sigma\,(1/r - 1/R) \qquad (5)$$

If r = 20.0 cm and R is only one percent larger, or = 20.2 cm, and a Plateau solution with $\sigma_{20°C}$ = 28.6 dyne/cm is used: ΔP = 0.057 dyne/cm^2 or 1000 times less than the excess pressure of each bubble. Thus the flow, in line with Eq. 3, becomes 1000 times slower. The total efflux time, until $r \rightarrow 0$, using our standard flow tube, becomes extremely long, but it can nevertheless be readily measured.

The mathematical relation is more complicated, as the volume, v, of the smaller sphere ($v_{start} = 4/3\pi r^3_{start}$) decreases and the volume, V, of the larger sphere ($V_{start} = 4/3\pi R^3_{start}$) increases.

Defining the constant ($R^3_{start} + r^3_{start}$) = A, the efflux time, $T_{o\text{-}o}$ is given by the integral:

$$T_{o\text{-}o} = \frac{8 \cdot l \cdot \eta}{\sigma \cdot \rho^4} \cdot \int_{r_{start}}^{r_{end}} \frac{r^3 \cdot \sqrt[3]{(A - r^3)}}{\sqrt[3]{(A - r^3)} - r} \cdot dr \qquad (6)$$

where ρ is the radius of the flow tube and the other parameters are as defined in Eqs. 3 and 4.

In this two-bubble experiment the pressure in one was made to oppose the other. The reverse situation prevails in the double bubble, as shown in Fig. 3. Plateau (*2*) and Boys (*4*) gave details on how to blow one or more bubbles inside one another. The outer bubble exerts pressure on the gas inside equal to $4\sigma/R$; the inner bubble is subjected, in addition to its own surface tension pressure of $4\sigma/r$, to that of the gas surrounding it so that the total excess pressure in the inner bubble, ΔP_i:

$$\Delta P_i = 4\sigma(1/R + 1/r) \qquad (7)$$

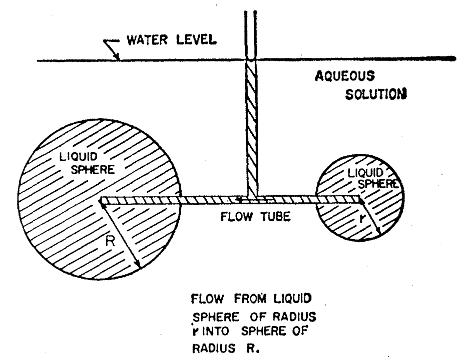

Fig. 4. Two liquid spheres suspended in an aqueous solution with a flow tube.

Two cases for efflux time have to be distinguished: whether the flow tube is attached to the inner bubble or the outer bubble. It would be too space-consuming to derive here the mathematical expression for the efflux times. Suffice to describe a simple case, when r is just slightly below R. By inserting my standard flow tube (but without the thistle) inside a small Plateau solution bubble I have blown into it a bubble of 7.5-cm radius, thereby expanding the outside bubble to slightly over this radius and thus obtaining a double bubble with a radius of 7.5 cm. The total efflux time was 860 seconds or exactly one half the value of Eq. 4 and in complete agreement with Eq. 7.

With two bubbles, their pressures can either diminish each other or reinforce each other. From this fact a large number of multibubble combinations can be devised, affording a large variety of instructive high school experiments.

The efflux time law, however, is not limited to soap bubbles; it also applies to spheres of liquids. Plateau (*2*) showed how an immiscible liquid can be suspended in another liquid of the same density and how, in the absence of gravity, it assumes the shape dictated only by the interfacial surface tension, σ_i, namely that of a sphere.

The efflux time of a liquid sphere is twice as long as that of a soap bubble (Eq. 4) since, in contrast to the two films here, we have only one interfacial film. Experiments were made to measure the total efflux time of a liquid *o*-toluidine (o-$CH_3 \cdot C_6H_4 \cdot NH_2$) sphere, suspended in an aqueous solution of NaCl of equal density at room temperature through a flow tube, and they confirmed the above statement. Since the viscosity of *o*-toluidine is about 200 times greater than that of

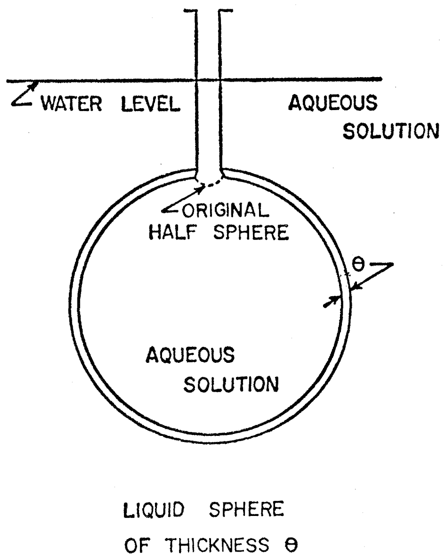

Fig. 5. Liquid sphere of thickness θ suspended in an aqueous solution with a blow tube.

air, while the interfacial tension of *o*-toluidine–salt solution at 20°C equals 30 dyne/cm, that is, about the same as our soap solutions, the efflux time for the same geometry is increased by a factor of 200.

These experiments are much more complicated to perform than those with a soap bubble and require gravity-free conditions (*8*).

The two-sphere case, shown in Fig. 4, however, is simple to demonstrate. Two spheres of *o*-toluidine, with radii R and r (between 5 and 1 cm), suspended in a solution of NaCl, were connected with a flow tube in the form of a T filled with *o*-toluidine. If the tips of the flow tube are covered with a thin layer of paraffin there is no difficulty in having the liquid spheres adhere to them; by coloring one sphere with an organic dye, I can observe the liquid flow. As in the case of soap bubbles, the larger sphere grows at the expense of the smaller one until the latter disappears and is converted into a flat film, sticking to the tip of the flow tube. The efflux time is in agreement with the theoretical one given by the integral 6, only $\sigma_i = \frac{1}{2} \cdot \sigma$.

With liquids one can also "blow" double spheres, one inside the other, as was shown by Plateau (*2*) and as seen in Fig. 5. Whereas soap bubbles have a practically infinite thinness of 10 to $\simeq$ 100 $\mu\mu$, the liquid double spheres can have any desired thickness, θ. By attaching a known volume, v, of, for example, *o*-toluidine at the end of a tube (by means of paraffin) and pouring water or salt solution slowly into this tube from a dropping funnel, the *o*-toluidine can be expanded first into a half-sphere (as indicated by the dotted half circle in Fig. 5) and, by adding more water, into a sphere of any desired size, surrounded by a thin sphere of *o*-toluidine of thickness, θ. By using 1.0 ml of *o*-toluidine I have been able to "blow" a water sphere 6.0 cm in diameter surrounded by a thin sphere of *o*-toluidine about 0.18 mm thick. Of course, such liquid film spheres are fragile and require great care in handling.

The efflux time of water (or any other suitable fluid) from such a thin film liquid sphere is given by Eq. 4, provided ΔP is doubled, since it has two interfacial tension surfaces. It can be more readily demonstrated and measured than any of the other liquid sphere cases, since the inside liquid, water, can be easily permitted to flow to the outside water reservoir by means of a flow tube covered on the outside with a thin paraffin layer. Care has to be taken so that its inlet is positioned in the center of the sphere; the "blow" tube also has to be progressively lowered to keep the flow tube inlet in the center of the water sphere. The observed efflux times confirm Eq. 4, although the accuracy attained was much less than that with soap bubbles.

So far I have discussed only the change with time of gaseous and liquid spheres. Such a study does not have to be limited to spheres. Plateau (*2*) and Boys (*4*) have shown that both soap-film and liquid cylinders can be produced; these are stable if their height is less than π times their diameter. In a cylinder, one of the radii of curvature is infinite. It follows from Laplace's equation that the ΔP of a soap cylinder equals $2\sigma/R$, or only one-half of that of a sphere of the same radius. As Boys has shown (*4*, pp. 52–62) the cylinder contracts to a surface of zero curvature, and thus zero pressure, or the catenoid of rotation. The efflux time of a cylinder to a catenoid has been measured; in contrast to a sphere where ΔP increases as it contracts, in this particular case the contraction becomes slower and slower, and finally stops when the zero curvature of the catenoid has been reached (*8*).

Cylinders can be connected with flow tubes to other cylinders, or spheres, or catenoids, and thus the number of combinations increase manifold. Only one combination might be mentioned since it permits the measurement of σ and η of liquids from their efflux time. If in Fig. 4 a liquid sphere of radius r is connected by a flow tube to a catenoid of rotation of suitable size, the efflux time will be given by Eq. 4 instead of the integral 6.

In summary, the measurement of time in experiments involving flows determined only by surface tension forces gives a sensitive method to study the influence of various factors, physical and particularly chemical, on these forces (*8*).

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9. I thank E. A. Nodiff, A. J. Saggiomo, and T. W. Hoffman for the preparation of pure 9,10-dibromostearic acid and A. D. Kirshenbaum for glassblowing.

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Farmington Meteorite: Cristobalite Xenoliths and Blackening

Abstract. *The Farmington chondrite contains two small xenoliths of granular cristobalite, each surrounded by a thin reaction rim of diopsidic clinopyroxene. Similarities between the blackened structure and drusy cavities, characteristic of this meteorite, and those of an experimentally heat-treated chondrite suggest that Farmington was reheated rather than shocked, but neither the exact stage in the history of this stone at which reaction rims developed around the xenoliths nor the source of the calcium necessary to form rim diopside have been established with certainty.*

Xenolithic structures are not uncommon in chondritic meteorites, but usually the xenoliths are similar in overall chemical composition and mineralogy to the material by which they