

agreement with experimental results available at present. It must be admitted that inaccuracies inherent in the available experimental data prevent a sharp quantitative comparison with theory. On the other hand, the assumption that the bonds are independent and that only those break which possess large amounts of po-

tential energy at the instant of ionization is verified when instrumental systematic errors are evaluated.

Note.—After this method of calculation had been formulated, the author learned that an independent treatment of this problem, however, only applicable to diatomic molecules, was presented by D. P. Stevenson and J. W. Otvos at the Consolidated Mass Spectrometer Group Meeting, New Orleans (May, 1950).

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On the Stability of Gas Bubbles in Liquid-Gas Solutions

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With the neglect of the translational motion of the bubble, approximate solutions may be found for the rate of solution by diffusion of a gas bubble in an undersaturated liquid-gas solution; approximate solutions are also presented for the rate of growth of a bubble in an oversaturated liquid-gas solution. The effect of surface tension on the diffusion process is also considered.

INTRODUCTION

THE stability of gas bubbles in a liquid-gas solution is of concern in several problems of physical interest. Among these may be mentioned the extinction of sound or light in water by air bubbles, and the diffusion of air into the bubbles formed in the cavitating flow of a liquid.¹

A gas bubble in a liquid-gas solution will grow or shrink by diffusion according as the solution is oversaturated or undersaturated. The resulting motion of the bubble boundary introduces a transport term in the diffusion equation which makes it very difficult to obtain an analytic solution. This effect of the motion of the medium on the diffusion process is neglected in the following analysis; the resulting approximation, however, is quite good. The physical reason for the accuracy of the approximation is that the concentration of dissolved gas in the liquid surrounding the bubble is much smaller than the gas density in the bubble, and the region in the solution around the bubble through which the diffusion process takes place is very soon much larger than the bubble itself. Under this circumstance, the size of the bubble is of little consequence so far as the configuration of the surrounding concentration in the solution is concerned. The bubble size is important only insofar as it determines the interfacial area across which the mass transfer between phases takes place.

A more significant effect on the accuracy of the numerical results obtained here arises from translatory motion of a gas bubble in a liquid. Consider, for example, the motion due to buoyancy of an air bubble of density ρ in water of density ρ' . The buoyant force is

$$F = (4\pi/3)g(\rho' - \rho)R^3,$$

¹ See M. S. Plesset, *J. App. Mech.* **16**, 277 (1949).

where g is the acceleration of gravity and R is the bubble radius. The terminal velocity of rise of the bubble, v , is attained when this force is balanced by the force of resistance which is given approximately by Rybczynski's formula² to be

$$F_R = 6\pi\mu'Rv \frac{2\mu' + 3\mu}{3\mu' + 3\mu},$$

where μ' is the coefficient of viscosity of the liquid and μ is the coefficient of viscosity of the gas. The terminal velocity is found at once and, since ρ/ρ' and μ/μ' are small, it has very nearly the value

$$v = (g/3)(\rho'/\mu')R^2.$$

Thus, an air bubble of radius $R = 10^{-3}$ cm has a terminal velocity of rise in water $v = 3 \times 10^{-2}$ cm/sec. Even this slow motion through the diffusion atmosphere around the bubble is sufficient to produce some slight acceleration of the diffusion process. Hence, the diffusion rates deduced here will be somewhat low.

A summary of the results is contained in Tables I, II and in Figs. 1-4.

MATHEMATICAL SOLUTION OF THE DIFFUSION PROBLEM

Let us suppose that at the initial time $t=0$ a spherical gas bubble of radius R_0 is placed in a liquid-gas solution in which the concentration of dissolved gas is uniform and equal to c_i . The solution will be assumed to be at constant temperature and pressure, and the dissolved gas concentration for a saturated solution at this temperature and pressure will be denoted by c_s . The center

² See H. Lamb, *Hydrodynamics*, 6th edition (Cambridge University Press, London, 1932), p. 601. Rybczynski's formula should be used here rather than Stokes' formula, since the latter applies strictly to a rigid sphere in a fluid medium.

TABLE I. Times for complete solution of air bubbles in water.

<i>f</i>	$R_0=10^{-3}$ cm			$R_0=10^{-2}$ cm		$R_0=10^{-1}$ cm	
	<i>T</i> (sec.)	T_A (sec.)	T_S (sec.)	$T_A \times 10^{-2}$ (sec.)	$T_S \times 10^{-2}$ (sec.)	$T_A \times 10^{-1}$ (sec.)	$T_S \times 10^{-1}$ (sec.)
0	1.05	1.25	1.17	1.25	1.24	1.25	1.25
0.25	1.44	1.67	1.46	1.67	1.64	1.67	1.66
0.50	2.21	2.50	1.96	2.50	2.41	2.50	2.49
0.75	4.58	5.00	2.99	5.00	4.60	5.00	4.95
1.00	∞	∞	6.63	∞	58.8	∞	580

The tabulated values are the times, in seconds, required for air bubbles to dissolve completely in air-water solutions at 22°C. R_0 is the initial radius of the bubble, f is the ratio of the dissolved concentration of air in the solution c_i to the dissolved concentration for a saturated solution c_s . T is time calculated from the complete solution of Eqs. (17) with surface tension neglected; T_A is the time calculated from the approximation to Eq. (17) given in Eq. (16) which also neglects surface tension; T_S is the time calculated including surface tension effects under the same approximation as is used in obtaining T_A so that the effects of surface tension are noted by comparison of T_S and T_A . It should be remarked that T and T_A are proportional to R_0^2 .

TABLE II. Times of growth of air bubbles in water from R_0 to $10R_0$.

<i>f</i>	$R_0=10^{-3}$ cm			$R_0=10^{-2}$ cm	
	<i>T</i> (sec.)	T_A (sec.)	T_S (sec.)	$T_A \times 10^{-2}$ (sec.)	$T_S \times 10^{-2}$ (sec.)
1.25	466	496	567	496	501
1.50	228	248	266	248	249
1.75	149	165	174	165	166
2.00	110	124	129	124	124
5.00	24.6	30.9	31.7	30.9	31.0

The tabulated values are the times, in seconds, required for air bubbles in an air-water solution at 22°C to grow from R_0 to $10R_0$. The ratio of the dissolved concentration to the dissolved concentration for a saturated solution is f ; T is calculated from complete solution of Eqs. (24) which neglects surface tension; T_A is calculated from the approximate solution of Eq. (23) which also neglects surface tension; and T_S is the time calculated with the same approximation except that the effect of surface tension is included.

of the gas bubble will be assumed to be at rest, and it will be taken as the origin of a spherical polar coordinate system. At any time $t > 0$ when the bubble radius is R , the dissolved gas concentration c at a point in the solution at a distance r from the origin is to be found from the diffusion equation

$$\partial c / \partial t = \kappa \Delta c, \tag{1}$$

where κ is the coefficient of diffusivity of the gas in the liquid. The transport term, $\mathbf{u} \cdot \Delta c$, in which \mathbf{u} is the velocity produced in the medium by bubble growth or shrinkage, has been omitted from the left-hand side of Eq. (1). A spherically symmetric solution, $c(r, t)$, of Eq. (1) is to be found which satisfies the following conditions:

$$c(r, 0) = c_i, r > R; \quad \lim_{r \rightarrow \infty} c(r, t) = c_s, t > 0; \tag{2a}$$

$$c(R, t) = c_s, t > 0. \tag{2b}$$

It is convenient to introduce the dependent variable

$$u = r(c - c_s) \tag{3}$$

in place of c so that Eq. (1) becomes

$$\partial u / \partial t = \kappa (\partial^2 u / \partial r^2), \tag{4}$$

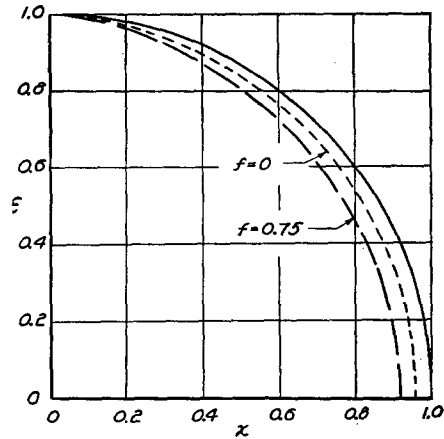


FIG. 1. Radius-time relation for dissolving bubbles neglecting surface tension. The ordinate, ϵ , is the ratio of the bubble radius to its initial radius, and the abscissa, x , is a dimensionless variable proportional to the square root of the time (compare Eq. (13)). The solid curve is the approximate quasi-static solution of Eq. (16) which, in this dimensionless form, gives the radius-time behavior for any type of gas bubble in any undersaturated solution. The dashed curves come from the more accurate Eqs. (17) and depend in form on the ratio of the saturated dissolved-gas concentration to the gas density (c_s/ρ); the value used in these curves is $c_s/\rho=0.02$, which is the value for an air-water solution at 22°C. f is the ratio of the initial dissolved-air concentration to the concentration at saturation.

with initial and boundary conditions

$$u(r, 0) = r\delta, \tag{5a}$$

$$u(R, t) = 0. \tag{5b}$$

The constant δ has, of course, the value $(c_i - c_s)$. One

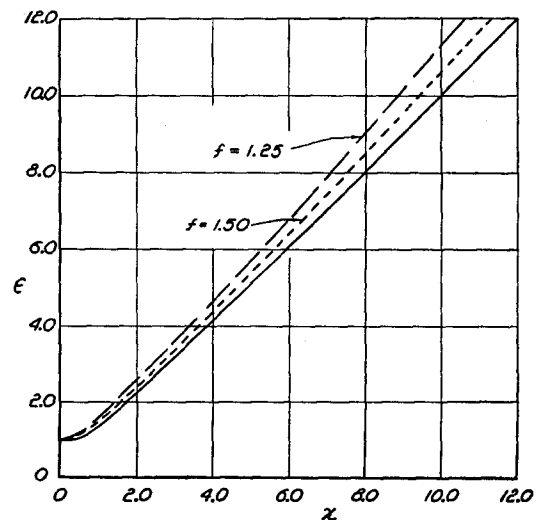


FIG. 2. Radius-time relation for growing bubbles neglecting surface tension. The solid curve is the approximate quasi-static solution of Eq. (23) and gives in dimensionless form the radius-time behavior for a bubble growing in any oversaturated solution. The dashed curves are the more accurate solution of Eqs. (24). The dimensionless variables ϵ and x are defined in Eq. (21); f is the ratio of the dissolved-gas concentration to the concentration at saturation. For the dashed curves, it has been assumed that $c_s/\rho=0.02$.

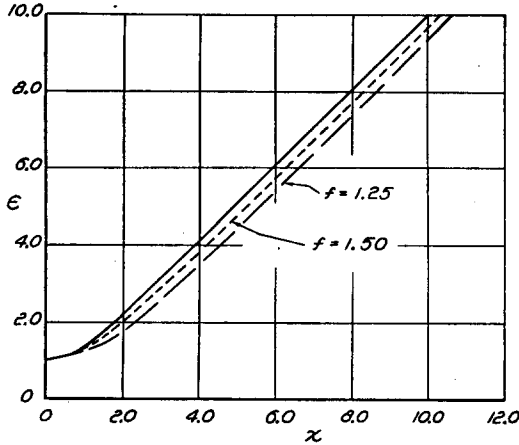


FIG. 3. Radius-time relation for dissolving bubbles with and without surface tension. The solid curve gives the radius-time behavior for a gas bubble in an undersaturated solution with surface tension neglected (Eq. (16)). The dashed curves include the effect of surface tension and are drawn for an initial bubble radius $R_0=10^{-3}$ cm; the surface tension constant is for an air-water combination, and $c_s/\rho=0.02$.

need only make a linear shift in the r -coordinate by

$$\xi=r-R$$

in order to make the problem identical with a familiar problem in heat conduction which has the solution³

$$u(r, t) = \frac{\delta}{2(\pi\kappa t)^{1/2}} \int_0^\infty (R+\xi') \{ \exp[-(\xi-\xi')^2/4\kappa t] - \exp[-(\xi+\xi')^2/4\kappa t] \} d\xi'. \quad (6)$$

The quantity of interest is the concentration gradient at $r=R$. One finds directly from (6) that

$$(\partial u/\partial r)_R = \delta \{ 1 + R/(\pi\kappa t)^{1/2} \};$$

and, since $(\partial c/\partial r)_R = (\partial u/\partial r)_R/R$, one has

$$\left(\frac{\partial c}{\partial r}\right)_R = \delta \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa t)^{1/2}} \right\}. \quad (7)$$

Thus, the mass flow into the bubble per unit time has the value

$$\frac{dm}{dt} = 4\pi R^2 \kappa \left(\frac{\partial c}{\partial r}\right)_R = 4\pi R^2 \kappa \delta \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa t)^{1/2}} \right\}. \quad (8)$$

Now Eq. (8) is a solution of the diffusion problem which is valid only for a stationary bubble boundary. It is, however, as has been discussed above, a reasonable physical approximation to use this result for a bubble boundary which changes in time by diffusion. Then, if ρ is the density of the gas in the bubble, one has

$$dm/dt = 4\pi R^2 \rho (dR/dt), \quad (9)$$

³ See, for example, H. S. Carslaw, *Introduction to the Mathematical Theory of the Conduction of Heat in Solids* (Dover Publications, New York 1945), p. 158.

so that, from Eq. (8),

$$\frac{dR}{dt} = \frac{\kappa\delta}{\rho} \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa t)^{1/2}} \right\}. \quad (10)$$

In addition to the coefficient of diffusivity, κ , the physical constants which enter are the ratio of the saturated dissolved gas concentration to the gas density

$$d = c_s/\rho,$$

and the ratio of the initial dissolved gas concentration to the concentration at saturation

$$f = c_i/c_s.$$

The differential Eq. (10) is readily solved, and the two cases of an undersaturated solution, $0 \leq f < 1$, and of an oversaturated solution, $f > 1$, will be considered separately.

Bubble Dissolving in an Undersaturated Solution

Equation (10) may be written in the form

$$\frac{dR}{dt} = -\alpha \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa t)^{1/2}} \right\} \quad (11)$$

where now α is a positive constant with the value

$$\alpha = \kappa(c_s - c_i)/\rho = \kappa d(1-f). \quad (12)$$

It is convenient to put Eq. (11) in dimensionless form. With

$$\epsilon = R/R_0, \quad x^2 = (2\alpha/R_0^2)t, \quad (13)$$

the differential equation becomes

$$d\epsilon/dx = -x/\epsilon - 2\gamma, \quad (14)$$

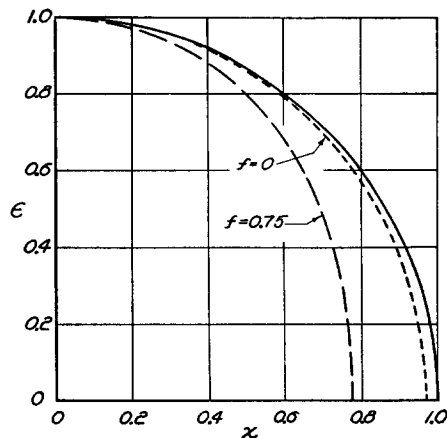


FIG. 4. Radius-time relation for growing bubbles with and without surface tension. The solid curve gives the radius-time behavior for a gas bubble in an oversaturated solution with surface tension neglected (Eq. (23)). The dashed curves include the effect of surface tension; for these curves the initial bubble radius has been taken to be 10^{-3} cm; the surface tension constant is that of an air-water combination; and $c_s/\rho=0.02$.

where

$$\gamma = \left(\frac{c_s - c_i}{2\pi\rho} \right)^{\frac{1}{2}} \tag{15}$$

It is to be noted that the constant γ is in general small compared to x/ϵ when enough time has elapsed for significant diffusion to take place, so that an approximate solution may be obtained by neglecting γ . This neglect is equivalent to omitting the second term of Eq. (11) in which the time appears explicitly. This approximate solution is

$$\epsilon^2 = 1 - x^2 \tag{16}$$

A solution to the complete equation may also be readily found. Since Eq. (14) is homogeneous, it is convenient to express the solution in parametric form. One then finds in a straightforward manner that

$$\epsilon = e^{-\gamma z} \{ \cos[(1-\gamma^2)^{\frac{1}{2}}z] - \gamma(1-\gamma^2)^{-\frac{1}{2}} \sin[(1-\gamma^2)^{\frac{1}{2}}z] \}; \tag{17a}$$

$$x = e^{-\gamma z} (1-\gamma^2)^{-\frac{1}{2}} \sin[(1-\gamma^2)^{\frac{1}{2}}z]. \tag{17b}$$

The scale of the parameter z has been fixed so that $z=0$ when $x=0$ and $\epsilon=1$. A comparison of the approximate solution (16) with the accurate solution (17) is given graphically in Fig. 1, and it is evident that the approximation is fairly good. Herein is contained a justification of the remark in the introduction that the diffusion concentration c is rapidly adjusted to a quasi-static distribution.

The time required for a bubble to dissolve completely is given from Eq. (16) by $x=1$, and from Eqs. (17) by $x = \exp[-\gamma(1-\gamma^2)^{-\frac{1}{2}} \cos^{-1}\gamma]$. In either case, the time for complete solution is proportional to R_0^2 . Some numerical values for times of complete solution are given in Table I for air bubbles in water where the constants have been fixed by taking $\kappa = 2 \times 10^{-5}$ cm² sec.⁻¹, and from the solubility of air at 22°C, $c_s/\rho = 0.02$.

Bubble Growth in an Oversaturated Solution

For this case, Eq. (10) may be written in the form

$$\frac{dR}{dt} = \alpha \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa t)^{\frac{1}{2}}} \right\} \tag{18}$$

where the positive constant α now has the value

$$\alpha = \kappa(c_i - c_s)/\rho = \kappa d(f-1). \tag{19}$$

The differential equation may again be put into dimensionless form

$$d\epsilon/dx = (x/\epsilon) + 2\gamma \tag{20}$$

by the substitutions

$$\epsilon = R/R_0; \quad x^2 = (2\alpha/R_0^2)t. \tag{21}$$

The constant γ now is given by

$$\gamma = \left(\frac{c_i - c_s}{2\pi\rho} \right)^{\frac{1}{2}} \tag{22}$$

The approximate solution obtained with the neglect of γ is

$$\epsilon^2 = 1 + x^2, \tag{23}$$

and the accurate solution of Eq. (20) is readily found to be

$$\epsilon = e^{\gamma z} \{ \cosh[(1+\gamma^2)^{\frac{1}{2}}z] + \gamma(1+\gamma^2)^{-\frac{1}{2}} \sinh[(1+\gamma^2)^{\frac{1}{2}}z] \}; \tag{24a}$$

$$x = e^{\gamma z} (1+\gamma^2)^{-\frac{1}{2}} \sinh[(1+\gamma^2)^{\frac{1}{2}}z]. \tag{24b}$$

A graphical comparison of the solutions given by Eq. (23) and Eqs. (24) is given in Fig. 2, and it is evident from both solutions that ϵ varies linearly with x when x is large. In fact, one finds from Eqs. (24)

$$\epsilon \approx [\gamma + (1+\gamma^2)^{\frac{1}{2}}]x, \quad \epsilon, x \gg 1. \tag{25}$$

A tabulation of the times of growth from R_0 to $10R_0$ for air bubbles in water at 22°C is presented in Table II.

EFFECT OF SURFACE TENSION ON THE DIFFUSION

If the surface tension constant for the given gas-liquid combination is σ , then the equation of state for a gas bubble of radius R in a liquid at pressure p , and temperature T , is

$$p + 2\sigma/R = (B/M)\rho(R)T \tag{26}$$

where $\rho(R)$ is the gas density in the bubble, M is the molecular weight of the gas, and B is the universal gas constant. Thus,

$$\begin{aligned} \rho(R) &= \frac{M}{BT} p + \frac{2M\sigma}{BT R} \\ &= \rho(\infty) + \tau/R, \end{aligned} \tag{27}$$

where $\rho(\infty)$ is the density of the gas under the same conditions of pressure and temperature with a gas-liquid interface of zero curvature, and

$$\tau = 2M\sigma/BT. \tag{28}$$

The mass of gas in the bubble is

$$m = \frac{4\pi}{3} R^3 \rho(R) = \frac{4\pi}{3} R^3 \rho(\infty) + \frac{4\pi}{3} R^2 \tau \tag{29}$$

so that

$$\frac{dm}{dt} = 4\pi R^2 \frac{dR}{dt} \left\{ \rho(\infty) + \frac{2\tau}{3R} \right\}. \tag{30}$$

Equation (30) now replaces Eq. (9). The equality of (8) and (30) gives the differential equation for the bubble radius

$$\frac{dR}{dt} = \frac{\kappa(c_i - c_s)}{\rho(\infty) + 2\tau/3R} \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa t)^{\frac{1}{2}}} \right\}. \tag{31}$$

The dissolved concentration, c_s , which is in equilibrium

with the gas density $\rho(R)$, is given by

$$c_s/\rho(R) = d, \quad c_s = [\rho(\infty) + \tau/R]d, \quad (32)$$

where the value of d is the same as that used in the previous formulation since it may be shown that d is not affected by surface tension effects. As before, the initial dissolved concentration, c_i , is conveniently expressed in terms of f by the relation

$$c_i/\rho(\infty) = fd. \quad (33)$$

Equation (31) may now be written

$$\frac{dR}{dt} = -\kappa d \frac{1-f + \tau/(R\rho(\infty)) \left\{ \frac{1}{R} + \frac{1}{(\pi\kappa d)^{\frac{1}{2}}} \right\}}{1 + 2\tau/(3R\rho(\infty))}, \quad (34)$$

and the following dimensionless variables

$$\epsilon = R/R_0, \quad x'^2 = (2\kappa d/R_0^2)t, \quad (35)$$

put this equation in the form

$$\frac{d\epsilon}{dx'} = -\frac{(1-f) + \delta/\epsilon \left\{ \frac{x'}{\epsilon} + 2b \right\}}{1 + 2\delta/3\epsilon}, \quad (36)$$

where

$$\delta = \tau/[R_0\rho(\infty)], \quad b = (d/2\pi)^{\frac{1}{2}}. \quad (37)$$

An approximate solution corresponding to Eqs. (16) and (23) except for the inclusion of surface tension is found by neglecting the small constant b in Eq. (36). This solution is

$$1 - \epsilon^2 - 2\delta \left[\frac{1}{1-f} - \frac{2}{3} \right] (1 - \epsilon) + \frac{2\delta^2}{1-f} \left[\frac{1}{1-f} - \frac{2}{3} \right] \ln \frac{\delta + (1-f)}{\delta + (1-f)\epsilon} = x'^2(1-f). \quad (38)$$

When $0 \leq f < 1$, one may put

$$x^2 = x'^2(1-f) \quad (39a)$$

in Eq. (38). The resulting function $\epsilon(x)$ when $R_0 = 10^{-3}$ cm is compared graphically in Fig. 3 with the corresponding solution without surface tension given by Eq. (16). The time of complete solution with surface tension is given in Table I for air bubbles in water, where as before the constants have the values $\kappa = 2 \times 10^{-5}$ cm² sec.⁻¹, $d = 0.02$.

When $f > 1$, the substitution

$$x^2 = x'^2(f-1) \quad (39b)$$

may be used in Eq. (38) and the resulting function $\epsilon(x)$ for $R_0 = 10^{-3}$ cm is compared graphically in Fig. 4 with the corresponding solution without surface tension given by Eq. (23). Numerical values for the growth of air bubbles in oversaturated water with the effect of surface tension included are given in Table II.

The special case $f = 1$ is of interest. If surface tension is neglected, a bubble of any radius would be stable against diffusion in a saturated solution. Such a bubble actually dissolves because of surface tension, and its behavior in time is found by putting $f = 1$ in Eq. (36). The solution with neglect of the term containing the constant b is

$$1 - \epsilon^3 + \delta(1 - \epsilon^2) = (3\delta/2)x'^2, \quad (40)$$

and the time to complete solution is given by

$$x'^2 = (2/3\delta)(1 + \delta). \quad (41)$$

Numerical values determined from Eq. (41) are given in Table I where the constants have the values appropriate for air bubbles in water at 22°C.