

## Solubility inversion effects on diffusion from collapsing bubbles

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**Abstract**—This work discusses the dissolution of gas bubbles in liquids subjected to a sudden pressure surge, as well as lending insight to studies on rectified diffusion. The bubble growth rates for rectified diffusion under isothermal conditions as predicted in previous studies are much lower than the rate found experimentally. The assumption of isothermal conditions can be justified only for infinite thermal diffusivity. For real gas bubbles collapsing in a large body of liquid, however, the thermal condition lies between the isothermal and adiabatic limits. Our analysis was undertaken to establish diffusion conditions for a collapsing cavity under the adiabatic limit. Contrary to the case of isothermal collapse, where the increased pressure (and hence the surface concentration) can result only in an outward diffusional flux, the solubility inversion effect for gases can cause first inward and then outward diffusional flux during the same phase of adiabatic collapse. In particular, when the heat of solution,  $\Delta H_s$ , of the gas is less than  $(\gamma BT_0)/(1 - \gamma)$ , (where  $\gamma = C_p/C_v$ , and  $B =$  gas constant), the diffusional flux changes direction at

$$R = R_0 \left[ \left( \frac{\gamma}{1 - \gamma} \right) \left( \frac{BT_0}{\Delta H_s} \right) \right]^{1/3(\gamma - 1)}$$

Even in situations where flux reversal does not occur, the net diffusional outflux during collapse is less in the adiabatic case than that in the isothermal case. Further descriptions of mass transfer from a bubble collapsing adiabatically in a large body of liquid are presented.

### 1. INTRODUCTION

THE PROBLEM treated in this paper is that of diffusion from bubbles collapsing non-isothermally in a large body of liquid. Recent reviews of problems of a similar nature have been given by Bankoff[1] on diffusion-controlled bubble growth and by Flynn[2] on cavitation dynamics. The latter review discusses cyclic bubble motion induced by the application of acoustic waves to the liquid. The process describing the net inflow of gas into a bubble undergoing cyclic motion is termed "rectified diffusion"[3, 4].

Previous studies [5, 6] on the growth of bubbles by rectified diffusion are based on the implicit assumption of isothermal conditions during bubble oscillation. This assumption is based partly on criteria developed for isothermal bubble collapse by Plesset and Zwick[7]. Plesset and Zwick obtained solutions to the field equations for collapsing bubbles using a perturbation technique and found that the bubble collapse would approach isothermal conditions if

$$\frac{\rho_g c_g R_0^2 \omega}{\rho_l c_l \alpha_l} \ll 1. \quad (1)$$

In Zwick's analysis, an approximation using the binomial expansion was made to obtain the solution, which consequently will be valid only for small thermal penetration thicknesses. It is difficult to meet the criteria for isothermal collapse for bubbles with large radii, as demonstrated by Hickling[8]; for bubbles with high gas pressures and densities; and for high acoustic frequencies, as given by Plesset[9]. Hence, bubbles collapsing under these latter conditions tend to approach adiabaticity. Further doubts about isothermal collapse conditions arise from numerous experimental observations, notably sono-luminescence and increased chemical reaction rates resulting from acoustic cavitation. In fact, the gas temperature in the bubble is expected to change during oscillation, and the thermal condition of the bubble should lie somewhere between isothermal and adiabatic. Only the time-average

temperature over a number of oscillations can be assumed to be relatively constant.

This non-isothermal bubble condition, then, should seriously affect the concentration boundary condition at the bubble wall, and the effect of temperature on this equilibrium concentration must be incorporated in the solution in order to obtain a more precise analysis. To determine the exact temperature, an additional simultaneous equation, that for the heat flux, must be solved. Rather than undertaking this latter task in this paper, we shall consider the other bound on the diffusional process by assuming adiabatic conditions for the bubble. Since the surface concentration increases with increasing pressure but decreases with increasing temperature during non-isothermal collapse, there are two competing factors which affect the surface concentration. This effect on the surface concentration will result in less mass diffusing out of the cavity during adiabatic collapse than during isothermal collapse, which should result in faster rectified diffusional growth rates under adiabatic collapse conditions. The predicted rectified diffusion growth rates assuming isothermal collapse are orders of magnitude smaller than the experimental growth rates observed by Eller[10]. Since the isothermal condition places a lower bound on the growth rate, the purpose of this paper is to place an upper bound on the process by considering diffusion during adiabatic collapse. Along with this phenomena, our results apply directly to the dissolution of gas bubbles in liquids subjected to sudden pressure surges.

2. SOLUBILITY INVERSION EFFECTS

The solubility of gases in liquids is given by Henry's Law, which relates the surface concentration to the partial pressure of the dissolved gas by the equation

$$C_s = HP_g \tag{2}$$

The Henry's Law constant,  $H$ , is a function of temperature, and is given by Hildebrand[11] as

$$H = H_0 \exp \left[ \frac{-\Delta H_s}{BT_0} \left( \frac{T_0}{T} - 1 \right) \right] \tag{3}$$

For gas-filled cavities undergoing adiabatic collapse in which only a negligible fraction of the gas content is diffusing out during any one cycle, the gas pressure inside the bubble may be closely approximated by the equation

$$P_g = P_{g0} \left( \frac{R_0}{R} \right)^3 \left( \frac{T}{T_0} \right) = P_{g0} \left( \frac{T}{T_0} \right) \psi^{-3} \tag{4}$$

where  $\psi = \frac{R}{R_0}$ .

Letting  $C_{s0} = H_0 P_{g0}$ , and  $C_s^* = C_s / C_{s0}$ , the dimensionless concentration  $C_s^*$  can be written as

$$C_s^* = \exp \left[ \frac{-\Delta H_s}{BT_0} \left( \frac{T_0}{T} - 1 \right) \right] \left( \frac{T}{T_0} \right) \psi^{-3} \tag{5}$$

For isothermal bubble collapse,  $C_s^*$  varies inversely as  $\psi$  to the third power, that is

$$C_s^* = \psi^{-3} \tag{6}$$

This means that the equilibrium concentration,  $C_s^*$ , will only increase when the bubble is compressed isothermally as shown in Fig. 1.

For adiabatic conditions, the temperature is given by

$$T = T_0 \left( \frac{R}{R_0} \right)^{-3(\gamma-1)} = T_0 \psi^{-3(\gamma-1)} \tag{7}$$

and  $C_s^*$  varies with  $\psi$  according to the equation

$$C_s^* = \exp \left[ \frac{-\Delta H_s}{BT_0} (\psi^{3(\gamma-1)} - 1) \right] \psi^{-3\gamma} \tag{8}$$

Differentiating with respect to  $\psi$ , we obtain

$$\frac{\partial C_s^*}{\partial \psi} = C_s^* \left[ \frac{-\Delta H_s}{BT_0} 3(\gamma-1) \psi^{3\gamma-4} - 3\gamma \psi^{-1} \right] \tag{9}$$

The radius at which the concentration reaches its minimum value occurs when  $\partial C_s^* / \partial \psi = 0$ , which is

$$\psi = \psi_{cr} = \left[ \frac{\gamma}{\gamma-1} \left( \frac{BT_0}{-\Delta H_s} \right) \right]^{1/3(\gamma-1)} \tag{10}$$

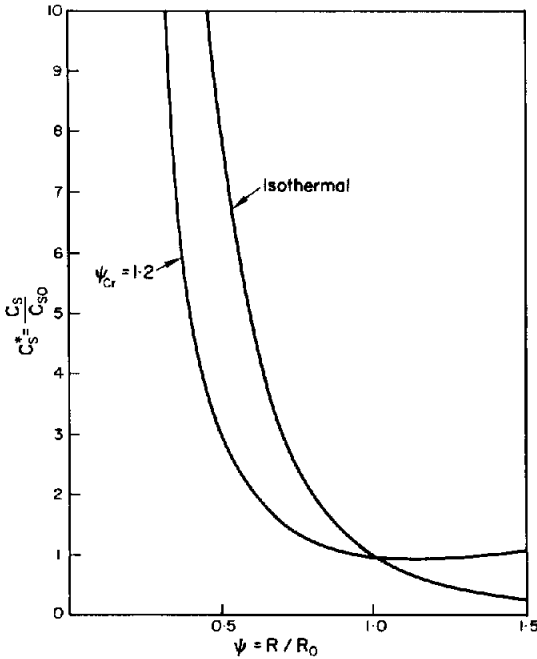


Fig. 1. Dimensionless surface concentration as a function of dimensionless bubble radius for  $\psi_{cr} > 1$ .

It is easily shown that for typical values of  $\gamma$  the second derivative of  $C_s^*$  with respect to  $\psi$  is always positive. Therefore,  $C_s^*$  reaches its minimum value at  $\psi = \psi_{cr}$ .

Consider the implications of  $C_s^*$  undergoing a minimum value at  $\psi_{cr}$ , when  $\psi_{cr}$  satisfies the following criteria:

$$\psi_{cr} > 1 \quad (11)$$

$$\psi_{cr} = 1 \quad (12)$$

$$\psi_{min} < \psi_{cr} < 1 \quad (13)$$

$$\psi_{cr} < \psi_{min} \quad (14)$$

In these relations,  $\psi_{min}$  is the dimensionless minimum radius reached during collapse.

(A) If  $\psi_{cr}$  is greater than unity,  $C_s^*$  will only increase when the bubble is compressed from its initial radius,  $R_0$ . Under these conditions the surface concentration for adiabatic collapse will always be less than that for isothermal collapse at the same radius. Consequently, less gas would diffuse out of the bubble during adiabatic col-

lapse than during isothermal collapse. A comparison of surface concentrations for isothermal and adiabatic collapse in which  $\psi_{cr} > 1$  is shown in Fig. 1.

(B) If  $\psi_{cr}$  is less than unity but greater than  $\psi_{min}$ , the equilibrium surface concentration  $C_s^*$  will initially decrease until  $\psi_{cr}$  is reached as the bubble is compressed. Upon further compression below  $\psi_{cr}$ , the surface concentration increases. As shown in Fig. 2, this behavior of the equilibrium concentration under adiabatic conditions is markedly different from that under isothermal conditions, where  $C_s^*$  can only increase during compression and only decrease during expansion. This peculiar behavior under adiabatic conditions is easily understandable if we recall that the solubility of gases decreases with increasing temperature and increases with increasing pressure [11, 12]. Thus, there are two competing factors which determine the equilibrium surface concentration during adiabatic collapse of bubbles, and the surface concentration will behave differently depending on the value of  $\psi_{cr}$ . In this figure the

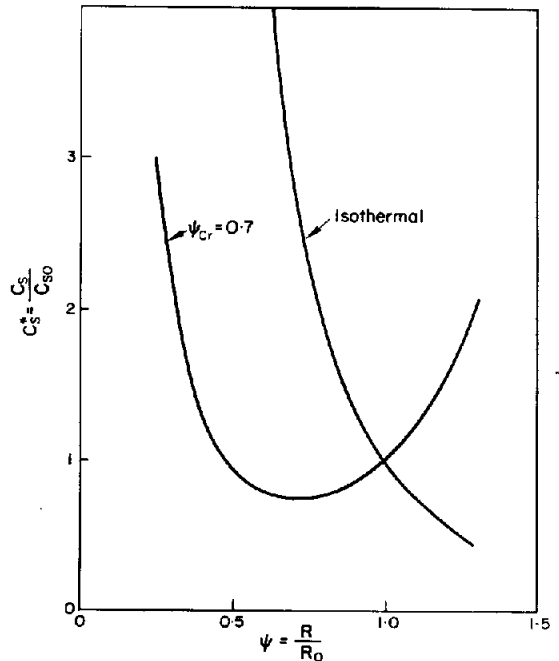


Fig. 2. Dimensionless surface concentration as a function of dimensionless bubble radius for  $\psi_{min} < \psi_{cr} < 1$ .

surface concentration's dependence on temperature during collapse dominates until  $R = 0.7 R_0$ , after which the surface concentration has a stronger dependence on the partial pressure of the solute gas inside the cavity.

(C) Consider next the case where  $\psi_{cr}$  is below the minimum radius reached during collapse. The minimum radius is a function of the amount of gas in the cavity at the initiation of collapse, the ratio of specific heats, and the change in the number of moles in this cavity during collapse. In Fig. 3 we observe that the surface concentration only decreases as the bubble collapses; as a result, the gas diffuses into the bubble during collapse. For the collapse of the bubble,  $C_s^*$  will only increase if  $\psi_{cr} \geq 1$ , and will only decrease if  $\psi_{cr} < \psi_{min} < 1$ .

(D) The case of  $\psi_{cr}$  equal to unity is of unusual interest, and the variation of  $C_s^*$  with  $\psi$  for this case is shown in Fig. 4. In this case  $C_s^*$  will only increase, whether the bubble is compressed or expanded from its initial radius. Consequently, the bubble will only dissolve if  $\psi_{cr} = 1$ ,

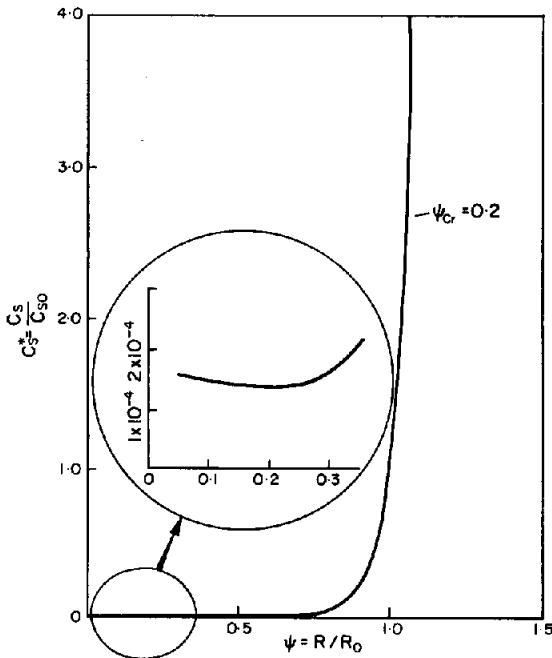


Fig. 3. Dimensionless surface concentration as a function of dimensionless bubble radius for  $\psi_{cr} < \psi_{min} < 1$ .

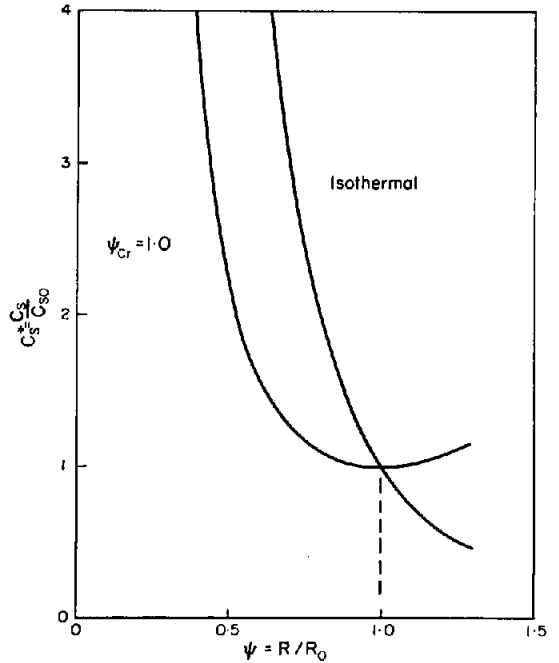


Fig. 4. Dimensionless surface concentration as a function of dimensionless bubble radius for  $\psi_{cr} = 1$ .

regardless of whether the bubble is compressed or expanded from its initial radius.

To further delineate these criteria, we shall now consider the case of the pure collapse of gas-filled cavities and determine the amount of diffusion from the bubble in any one complete cycle.

### 3. EQUATIONS OF MOTION

We shall briefly review the development of the equations describing bubble motion. For a gas-filled cavity collapsing in an incompressible liquid, the liquid phase continuity equation in spherical coordinates is

$$\frac{\partial(r^2V)}{\partial r} = 0. \tag{15}$$

For no evaporation or condensation on the cavity wall, Eq. (15) can be integrated to give

$$r^2V = f(t) = R^2\dot{R}. \tag{16}$$

In the absence of body forces and external temperature effects, the momentum balance gives

$$\rho \frac{\partial V}{\partial t} + V \frac{\partial V}{\partial r} = -\frac{\partial P}{\partial r} - |\nabla \cdot \bar{\tau}|_r \quad (17)$$

Substitution for  $V$  from Eq. (16) into Eq. (17) and integrating between the limits  $r = R$  and  $r = \infty$  gives the following dynamic equation governing the collapse of the cavity:

$$R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{P_l(R) - P_\infty}{\rho} \quad (18)$$

It is noted that the divergence of stress tensor is zero for a Newtonian fluid, and  $P_l(R)$  is given by the force balance as

$$P_l(R) + \bar{\tau}_{rr,l} + \frac{2\sigma}{R} = P_g + \bar{\tau}_{rr,g}$$

For negligible spatial variation in density inside the cavity, it has been shown by Fogler[13] that the above equation can be put in the form

$$R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{P_g - P_\infty}{\rho_l} - \frac{2\sigma}{R\rho} - \frac{\dot{R}}{R\rho} (4\mu_l + 3\kappa) \quad (19)$$

Since for ideal gases the dilational viscosity is zero, and for large or moderate size bubbles the viscous and surface tension effects are negligible, Eq. (19) reduces to

$$R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{P_g - P_\infty}{\rho} \quad (20)$$

Defining new dimensionless variables

$$\tau = \frac{t}{t_c}, \text{ where } t_c = R_0 \sqrt{\rho/P_\infty}$$

and 
$$\psi = \frac{R}{R_0}$$

Equation (20) can be written in the form

$$\psi \ddot{\psi} + \frac{3}{2} \dot{\psi}^2 = \frac{P_g - P_\infty}{P_\infty} \quad (21)$$

#### 4. DIFFUSION EQUATIONS

Next we shall consider the diffusion of the gas in the liquid to and from the gas bubble which is undergoing either collapse or radial oscillation. The diffusion equation in spherical coordinates is

$$\frac{\partial C}{\partial t} + V \frac{\partial C}{\partial r} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) \quad (22)$$

The radial velocity,  $V$ , in this equation can be obtained from Eq. (16).

The following dimensionless parameters transform the original equation from the spherical Eulerian coordinate system to Lagrangian coordinates:

$$h = \frac{r^3 - R^3}{R_0^3} = \left[ \left( \frac{r}{R_0} \right)^3 - \psi^3 \right] \quad (23)$$

$$\phi = \frac{9Dt_c}{R_0^2} \int_0^\tau \psi^4(\tau') d\tau' \quad (24)$$

and

$$\frac{\partial U}{\partial h} = \frac{C - C_0}{C_0} \quad (25)$$

Thus, Eq. (22) can be transformed to

$$\frac{\partial^2 U}{\partial \phi \partial h} = \frac{\partial}{\partial h} \left( \frac{r^4}{R_0^4} \frac{1}{\psi^4} \frac{\partial^2 U}{\partial h^2} \right) \quad (26)$$

Upon integrating Eq. (26) with respect to  $h$  and rearranging, we obtain

$$\frac{\partial U}{\partial \phi} = \left( 1 + \frac{h}{\psi^3} \right)^{4/3} \frac{\partial^2 U}{\partial h^2} \quad (27)$$

The transformed initial and boundary conditions are as follows:

Initial condition

$$U(h, 0) = 0.$$

Boundary conditions

$$(A) \frac{\partial U}{\partial h}(0, \phi) = \frac{C_s(\phi) - C_0}{C_0} \quad (28)$$

$$(B) \frac{\partial U}{\partial h}(\infty, \phi) = 0.$$

The diffusion into the bubble is given by

$$\frac{dn}{dt} = 4\pi R^2 D \left. \frac{\partial C}{\partial R} \right|_{r=R} \quad (29)$$

or

$$\frac{dn}{dt} = \frac{4}{3} \pi C_0 R_0^3 \frac{\partial U}{\partial t}(0, t). \quad (30)$$

5. DISCUSSION

The equations of motion (21) and diffusion (27) are coupled through the dimensionless radius  $\psi$  and the gas pressure  $P_g$ . However, since the change in the mass of the gas in the bubble is very small during any one cycle of collapse and rebound, it can be considered constant for that cycle, thus enabling the gas pressure to be evaluated from the ideal gas law. As a result, the bubble radius at any time,  $t$ , can be determined directly from the equation of motion. Solutions to the diffusion equations can now be readily obtained once the radius-time functionality has been established. Accordingly, the numerical scheme outlined in the appendix was carried out and the typical results obtained are discussed below.

Figures 5-7 present the dimensionless radius, dimensionless concentration driving force, and diffusional flux at different values of dimensionless time. Figure 5 shows that, for  $\psi_{cr} = 0.7$ , the dimensionless surface concentration difference initially decreases and reaches a minimum when  $\psi$  approaches 0.7. Upon further collapse below  $\psi_{cr}$ , the pressure dependence is dominant in the surface concentration relationship, causing  $C_s^*$  to increase and reach a maximum value at  $\psi_{min}$ . Similarly, during the rebound, the concentration first decreases until  $\psi_{cr}$  is reached, after which the concentration again increases.

The effect of this changing surface concentration on the concentration profile within the liquid is shown in Fig. 6. The dimensionless concentration difference of the solute gas is shown as a function of the radius,  $r$ , in the liquid at various

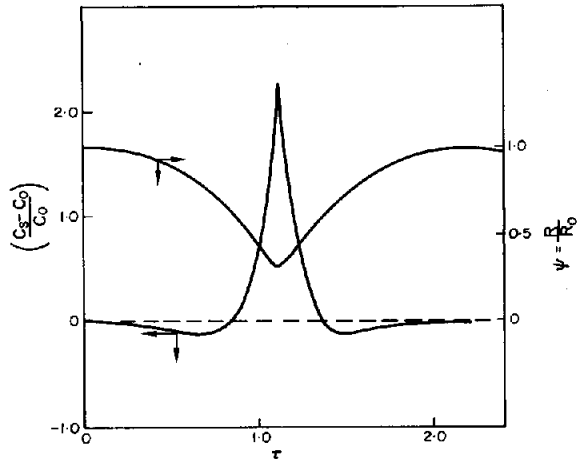


Fig. 5. Dimensionless concentration driving force and bubble radius as a function of time for  $\psi_{min} < \psi_{cr} < 1$ .

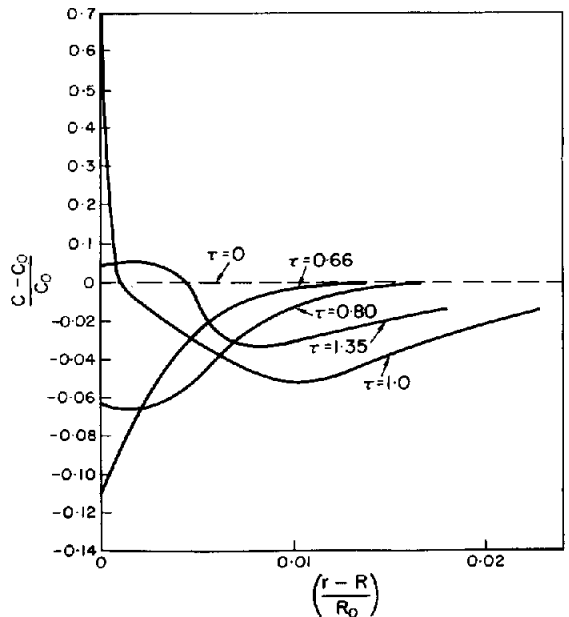


Fig. 6. Dimensionless concentration profile at various times during collapse for  $\psi_{min} < \psi_{cr} < 1$ .

times. Initially the dimensionless concentration difference is zero throughout the liquid. At time  $\tau = 0.66$  the surface concentration and the concentration at points close to the surface have decreased below the initial concentration resulting in diffusion of gas into the bubble. The shape

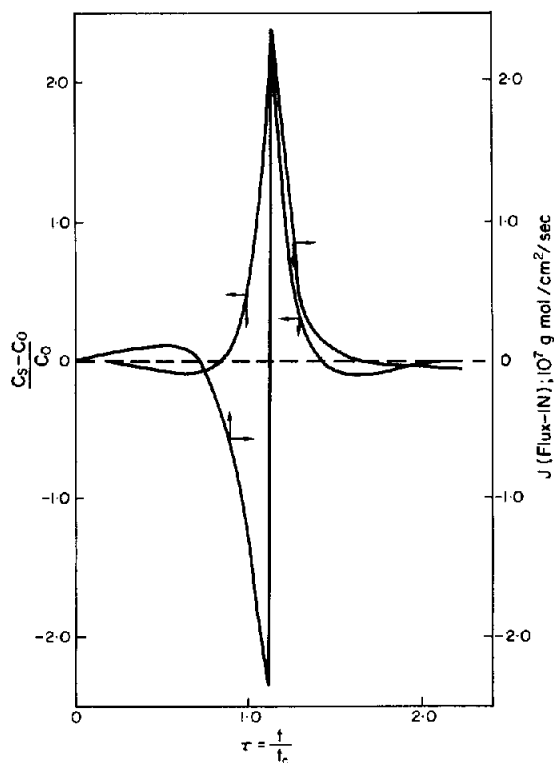


Fig. 7. Mass flux and dimensionless concentration driving force as a function of time showing flux reversal during the collapse for  $\psi_{\min} < \psi_{cr} < 1$ .

of this profile remains essentially the same until  $\tau = 0.68$ , when  $\psi_{cr}$  is approached. After  $\psi_{cr}$  is passed, the concentration on the bubble surface is higher than that at the points in the immediate vicinity of the surface, resulting in diffusion from the bubble into the liquid as shown by the profile for  $\tau = 0.8$ . At this same time the concentration at large distances from the bubble surface is at its initial value, and consequently one observes a minimum in the concentration out in the liquid. The concentration profile flattens rather rapidly in this region owing to the diffusion to this minimum from both sides of this region. Similar curves for other time intervals are also shown in this figure.

Figure 7 shows the mass flux as a function of time. As discussed above and shown in this figure, the flux is inward until a  $\psi_{cr}$  is reached; at  $\psi_{cr}$ , it is zero; and from  $\psi_{cr}$  to  $\psi_{\min}$  it is increas-

ingly outward owing to the change in sign in the concentration driving force. During the initial rebound period, the flux is inward as the surface concentration is decreasing until  $\psi_{cr}$  is again reached, and then the flux is outward as is predicted by the concentration profile.

Figure 8 presents the dimensionless concentration driving force, defined by Eq. (28A), as a function of the bubble radius, while Fig. 9 gives the flux as a function of dimensionless radius. Figures 8 and 9 correspond to the case of iso-

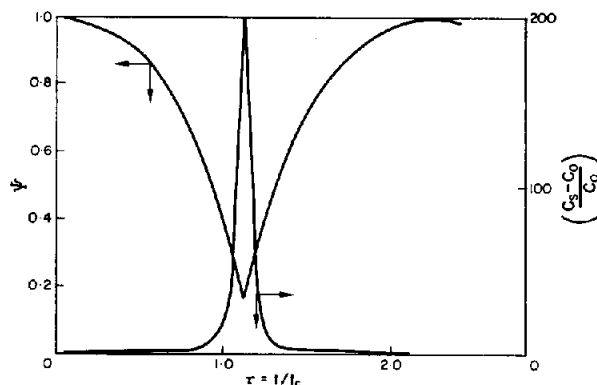


Fig. 8. Dimensionless concentration driving force and bubble radius as a function of dimensionless time for one cycle of isothermal oscillation.

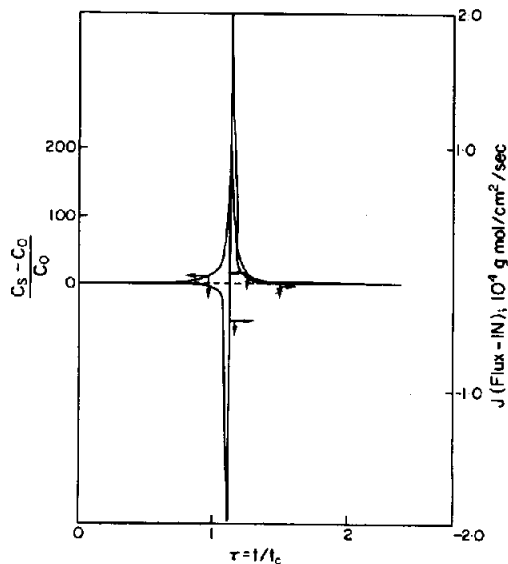


Fig. 9. Mass flux into the bubble and dimensionless concentration driving force as a function of dimensionless time for one complete cycle of isothermal oscillation.

thermal collapse for conditions otherwise exactly the same as those presented for adiabatic collapse in Figs. 5–7. Comparisons of Fig. 8 with Fig. 5 and of Fig. 9 with Fig. 7 clearly point out the differences existing between the oscillations of an isothermal and an adiabatic bubble. In adiabatic collapse, the concentration driving force, defined by Eq. (28A), goes through a minimum and is negative at this point as shown in Fig. 5; whereas, in the isothermal case, this driving force is always positive as shown in Fig. 9. Consequently, in the adiabatic collapse phase for the conditions  $\psi_{min} < \psi_{cr} < 1$ , the flux is first inwards and then outwards and vice-versa for the expansion phase. By contrast, one will note that the flux is always outwards during the isothermal collapse phase (and vice-versa for the expansion phase). The net change in mass of the bubble during one complete cycle of oscillation was thus found to be significantly different. A bubble, with an initial radius of  $10 \mu$ , gained a net mass of  $10^3$  molecules in one cycle of oscillation under adiabatic conditions with a  $\psi_{cr}$  of 0.7; while for one cycle of isothermal oscillation, the bubble lost a net mass of  $10^5$  molecules for otherwise similar conditions.

The above analysis clearly indicates that the temperature effect on the solubility is significant. The adiabatic collapse condition represents one bound, and the isothermal condition the other. The actual thermal condition of the bubble will, of course, be somewhere between these two extremes. When the changes in the bubble size are slow, the thermal collapse condition will be closer to isothermal; when these changes are rapid, the condition will be closer to adiabatic. Thus, during the initial stages of bubble collapse, the temperature will not change significantly; but during the later phase of collapse, the conditions approach adiabaticity [2].

As a result of the solubility inversion effect, the present theory predicts that less mass will diffuse out of the cavity during the latter phases of collapse than does the previous isothermal theory. Consequently, since adiabatic conditions predict a smaller net loss of mass during collapse than do the isothermal conditions, rectified dif-

fusion bubble growth would be faster under adiabatic collapse conditions than under isothermal conditions. As has already been mentioned, higher growth rates have been observed by Eller than those predicted by theory for isothermal collapse conditions.

Application of the foregoing theory to studies on the dissolution of gas bubbles in liquids subjected to a sudden pressure surge would indicate that the bubbles undergoing adiabatic collapse would require a longer time to dissolve than bubbles collapsing isothermally. This is a consequence of the lower surface concentration during oscillation for the adiabatic case. In fact, for certain values of  $\psi_{cr}$ , the bubbles undergoing adiabatic oscillation can have a net increase in the number of molecules in one cycle of oscillation, while the isothermal oscillation only results in dissolution of the bubble. This is readily seen by comparing Figs. 7 and 9. For the conditions of Fig. 7, the calculations show that there was a net increase of  $10^3$  molecules for one cycle, while for isothermal oscillation there was a net decrease of  $10^5$  molecules. For other values of  $\psi_{cr}$ , there may not be a net increase in the number of molecules during the adiabatic cycle; however the efflux of gas from the bubble will not be nearly so great as predicted by isothermal behavior.

## 6. SUMMARY

A study of diffusion from cavities collapsing adiabatically in a large body of liquid has been performed. Previous investigations have considered only isothermal collapse, while the thermal condition during collapse actually lies between the limits of adiabatic and isothermal collapse. Contrary to the case of isothermal collapse, in which the increased pressure (and thus the surface concentration) can only result in an outward diffusional flux, the solubility inversion effect for gases can cause first inward and then outward diffusional flux during adiabatic collapse. As a result of the competing effects of the temperature and the pressure on the solubility of the gas, a minimum value of the gas solubility is obtained at a certain "critical" radius of the bubble. This critical radius depends on the heat



of solution, the ratio of the specific heats, and the initial temperature of the gas. If the critical radius is smaller than the initial radius of the bubble, the gas will diffuse into the bubble during collapse until the critical radius is reached, beyond which the gas will diffuse out of the bubble. If the critical radius is greater than the initial radius, gas will diffuse only out of the bubble during adiabatic collapse; however, this net amount diffusing out will be less than that for collapse under isothermal conditions. Other criteria delineating the diffusion phenomena during adiabatic collapse are discussed in the paper.

## NOTATION

$B$	ideal gas law constant, cal g-mole <sup>-1</sup> °K <sup>-1</sup>
$c$	heat capacity, cal g <sup>-1</sup> °K <sup>-1</sup>
$C$	concentration of dissolved gas in the liquid, g-mole cm <sup>-3</sup>
$C_s^*$	dimensionless surface concentration
$D$	diffusivity of gas in the liquid, cm <sup>2</sup> sec <sup>-1</sup>
$h$	transform variable, defined by Eq. (23)
$H$	Henry's Law constant, g-mole g <sup>-1</sup> cm <sup>-2</sup> sec <sup>2</sup>
$\Delta H_s$	heat of solution of gas, cal g-mole <sup>-1</sup>
$n$	number of moles of gas in the bubble, moles
$P$	pressure, g cm <sup>-1</sup> sec <sup>-2</sup>
$r$	spatial coordinate, cm
$R$	bubble radius, cm

$\dot{R}$	velocity of bubble wall
$t$	time, sec
$t_c$	Rayleigh collapse time, sec
$T$	temperature, °K
$V$	radial velocity, cm sec <sup>-1</sup>
$U$	transform variable defined by Eq. (25)

## Greek symbols

$\alpha$	thermal conductivity, g cm sec <sup>-3</sup>
$\gamma$	ratio of specific heat for gas
$\kappa$	dilational viscosity, g cm <sup>-1</sup> sec <sup>-1</sup>
$\mu$	viscosity, g cm <sup>-1</sup> sec <sup>-1</sup>
$\phi$	transform variable, defined by Eq. (24)
$\rho$	density of liquid, g cm <sup>-3</sup>
$\psi$	dimensionless radius
$\sigma$	surface tension, g sec <sup>-2</sup>
$\bar{\tau}$	dimensionless time
$\tau$	stress tensor, g cm <sup>-1</sup> sec <sup>-2</sup>
$\tau'$	dummy integration variable
$\omega$	frequency of sound waves, sec <sup>-1</sup>

## Superscripts

• For time derivatives

## Subscripts

$0$	for initial conditions
$s$	for surface conditions
$cr$	for critical conditions
$min$	for minimum conditions
$g$	for gas
$l$	for liquid

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## APPENDIX

for  $2 \leq i \leq M-1$ 

## Numerical Technique

The equation of bubble motion (21) was solved using a sixth order corrector-predictor formula; the values of  $C_i^*$  corresponding to various  $\psi$  were calculated and stored. The diffusion equation was solved using an implicit (Crank-Nicholson)[14] method which results in the following tri-diagonal equations (for  $n > 0$ ):

$$-U_{1,n+1} + U_{2,n+1} = 2\Delta h \frac{C_t - C_i}{C_i} + U_{1,n} - U_{2,n} \dots \quad (1A)$$

$$U_{i-1,n+1} - (2 + \lambda_{n+1})U_{i,n+1} + U_{i+1,n+1} = -U_{i-1,n} + (2 - \lambda_{n+1})U_{i,n} - U_{i+1,n} \quad (2A)$$

$$\text{where } \lambda_{n+1} = \frac{2(\Delta h)^2 R_0^2}{9(\psi_{n+1}^3 + h)^{4/3} t_c D \Delta t} \quad (3A)$$

$$U_{M-1,n+1} - U_{M,n+1} = -U_{M-1,n} + U_{M,n} \quad (4A)$$

Equation (1A) represents the boundary condition at the bubble wall and Eq. (4A) that at infinity. The maximum value of  $h$  was fixed an order of magnitude greater than the diffusion thickness ( $\delta = \sqrt{D t_{\max}}$ ) to assure very little change in concentration at the point approximating the point at infinity.

The above numerical scheme can easily be shown to be stable and convergent for all values of  $\lambda$  as long as  $\Delta t$  and  $\Delta h$  both tend to zero.

**Résumé**—Cet article étudie la dissolution de bulles gazeuses dans des liquides soumis à une hausse soudaine de pression, et conduit également à donner un aperçu des travaux sur la diffusion rectifiée. Les taux de formation des bulles pour une diffusion rectifiée dans des conditions isothermiques, prévus dans des études antérieures, sont beaucoup plus faibles que le taux déterminé expérimentalement. L'hypothèse de conditions isothermiques ne peut être justifiée que pour une diffusivité thermique infinie. Pour des bulles gazeuses réelles se dissolvant dans une grande masse liquide, la condition thermique repose toutefois entre les limites isothermiques et adiabatiques. Notre analyse a été effectuée en vue d'établir les conditions de diffusion d'une cavité qui s'effondre sous l'effet de la limite adiabatique. Au contraire de l'effondrement isothermique où la pression accrue (et donc la concentration en surface) peut résulter seulement en un flux diffusif vers l'extérieur, l'effet d'inversion de solubilité pour les gaz peut causer un flux diffusif tout d'abord vers l'intérieur, puis vers l'extérieur, pendant la même phase d'effondrement adiabatique. En particulier, quand la chaleur de la solution,  $\Delta H_s$ , du gaz est inférieure à  $(\gamma B T_0)/(1-\gamma)$ , (dans laquelle  $\gamma = C_p/C_v$ , et  $B =$  constante du gaz), le flux diffusif change de sens à

$$R = R_0 \left[ \left( \frac{\gamma}{1-\gamma} \right) \left( \frac{B T_0}{\Delta H_s} \right) \right]^{1/3(\gamma-1)}$$

Même dans les cas où le renversement du flux ne se produit pas, le courant diffusif externe net, pendant l'effondrement, est plus faible dans le cas adiabatique que dans le cas isothermique. D'autres descriptions du transfert de masse à partir d'une bulle explosant adiabatiquement dans une grande masse de liquide sont présentées.

**Zusammenfassung**—Dieser Artikel erörtert die Lösung von Gasblasen in Flüssigkeiten, die einem plötzlichen Druckanstieg unterworfen werden und gibt Aufschluss über Studien an rektifizierter Diffusion. Die Blasenwachstumsraten für rektifizierte Diffusion unter isothermischen Bedingungen, die in früheren Studien vorausgesagt wurden, sind viel niedriger als die versuchsmässig gefundene Rate. Die Annahme isothermer Bedingungen kann nur für unbegrenztes thermisches Diffusionsvermögen gerechtfertigt werden. Für tatsächliche Gasblasen, die in einer grossen Flüssigkeitsmenge zusammenbrechen, befindet sich jedoch der thermische Zustand zwischen isothermischen und adiabatischen Grenzen. Unsere Analyse hatte das Ziel die Diffusionsbedingungen für ein zusammenbrechenden Hohlraum unter der adiabatischen Grenze festzustellen. Im Gegensatz zu dem Fall des isothermischen Zusammenbruchs, wo der erhöhte Druck (und damit die Oberflächenkonzentration) nur eine auswärts gerichtete Diffusionsströmung ergeben kann, kann der Löslichkeitsumkehrungseffekt für Gase zunächst einwärts und dann auswärts gerichtete Diffusionsströmungen während der gleichen Phase von adiabatischem Zusammenbruch bewirken. Wenn die Lösungswärme  $\Delta H_s$  des Gases geringer ist als  $(\gamma B T_0)/(1-\gamma)$ , (worin  $\gamma = C_p/C_v$ , und  $B =$  Gaskonstante), ändert die Diffusionsströmung ihre Richtung bei

$$R = R_0 \left[ \left( \frac{\gamma}{1-\gamma} \right) \left( \frac{B T_0}{\Delta H_s} \right) \right]^{1/3(\gamma-1)}$$

Sogar in Situationen, wo die Umkehrung der Strömung nicht stattfindet, ist doch die Netto Diffusionsströmung auswärts während des Zusammenbruchs geringer im adiabatischen, als im isothermischen, Fall. Es werden weitere Beschreibungen der Stoffübertragung aus einer in einer grossen Flüssigkeitsmenge adiabatisch zusammenbrechenden Blase dargelegt.