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Diffusion-controlled growth of multi-component gas bubbles

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Theoretical solutions for some important problems involving diffusion-controlled growth of gas bubbles in liquids in conditions of spherical symmetry are presented. It is shown that bubbles in systems containing several independently diffusing gases always approach an asymptotic composition and a parabolic relation between size and time. Solutions for this asymptotic regime have been obtained analytically for growth from zero size and numerically for growth from finite initial size; the two solutions agree well for sufficiently large sizes. The numerical methods can deal with transient growth from finite size, including the behaviour of bubbles of non-equilibrium initial composition. The differences between initial and equilibrium compositions make it easy to understand why the transient behaviour of bubbles can involve an initial period of shrinkage before the asymptotic regime is established.

1. Introduction

Experiments have shown that bubbles in glass melts often contain two or more gases and that their compositions generally change with time. Understanding of refining and of the action of refining agents requires the investigation of multicomponent bubbles, see Cable [1]. Progress in this area has been slow because good experimental data are scanty and because of difficulties in solving the theoretical problems: the latter can be simplified by assuming spherical symmetry but this is difficult to attain experimentally. The shapes of radius–time curves for growing or dissolving bubbles have often been claimed to show that the process is controlled by diffusion of gas in the melt, see for example Greene and co-authors [2–5]. However, this interpretation has been based on rather crude theoretical models involving one or more dubious basic assumptions. A more reliable indication of control by diffusion in the melt is the increase in rate of dissolution observed by Greene and Lee [4] when a bubble previously kept stationary was allowed to rise freely.

Most published theoretical studies have been conceived to deal with bubbles containing only one component although the need for models capable of dealing with more gases was recognized by Cable [6]; some of the more important studies have been by Epstein and Plesset [7], Readey and Cooper [8], Cable and Evans [9], Duda and Vrentas [10, 11]. The limitations of several of these approximations have been demonstrated by Frade [12] who showed that it is possible as well as very desirable to test numerical methods against analytical solutions for growth from zero initial size. These analytical solutions have long been available for one-component spheres but are here extended to multi-component bubbles. The validation of numerical solutions by comparison with the equivalent analytical ones requires computation of large increases in size, which cannot be done efficiently without sequential optimization of time steps.

Approximate quasi-stationary solutions have been suggested to deal with diffusion-controlled behaviour of gas bubbles in liquids, see, for example, Krämer [13]. Weinberg and Subramanian [14] found reasonable agreement with finite difference solutions for two cases involving bubbles in glass melts. Griffin [15] also used numerical methods to predict the behaviour of carbon dioxide–oxygen bubbles in water and found good agreement with experimental data. However none of these techniques was tested for accuracy against analytical solutions. Also the number of particular cases reported by those authors was insufficient to assess the overall performance of their finite difference methods.

The present work was undertaken to investigate the possibility of deriving analytical solutions for any problems involving the growth of multi-component bubbles and thus extend the range of tests available for numerical methods. Computation had shown that for a particular composition of multi-component bubble the radius increased linearly with the square root of time, and the composition was independent of time. The growth rate parameter could be expressed in terms of the properties of the system. These solutions proved to be closely related to the analytical solutions of Scriven [16] for growth of one-component spheres from zero size, and thus considerably extend the possibilities of rigorously testing finite difference procedures.

2. Statement of the problem

We consider a spherical bubble in an infinite body of uniform liquid. Spherical symmetry is maintained and the bubble contains a mixture of n independently diffusing gases which may differ in both solubility and diffusivity. Diffusivities are independent of

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concentration, and equilibrium according to Henry's law is maintained at the gas–liquid interface; temperature and pressure are constant. The gases in the bubble behave ideally so that their total molar concentration in the bubble is constant at c_s. Possible effects of viscosity or inertia of the liquid, surface tension and interfacial reaction kinetics are ignored. As the densities of the gases are much smaller than that of the liquid, the volume and density of the liquid may be assumed independent of dissolved gas concentration.

Given these conditions, a material balance for one solute in the liquid reduces to

$$D\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}D\frac{\partial c}{\partial r} - \left(\frac{a}{r}\right)^2 \frac{\mathrm{d}a}{\mathrm{d}t}\frac{\partial c}{\partial r} = \frac{\partial c}{\partial t} \qquad (1)$$

where c and D denote the concentration and diffusivity of the gas in the liquid, r is radial distance from the centre of the sphere and t is time. The flux of gas into the bubble of radius a is given by $D(\partial c/\partial r)_a$, hence

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{4}{3}\pi a^3 c_s\right) = 4\pi a^2 D\left(\frac{\partial c}{\partial r}\right)_a \qquad (2)$$

If a bubble contains n independently diffusing gases each of them is subject to an equation of the same form at Equation 1, but Equation 2 must be replaced by

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\tfrac{4}{3}\pi a^3 g_i c_s\right) = 4\pi a^2 D_i\left(\frac{\partial c_i}{\partial r}\right)_a \qquad (3)$$

where g_i is the mole fraction of Gas i in the bubble. Performing the differentiation indicated yields

$$g_i\frac{\mathrm{d}a}{\mathrm{d}t} + \frac{a}{3}\frac{\mathrm{d}g_i}{\mathrm{d}t} = \frac{D_i}{c_s}\left(\frac{\partial c_i}{\partial r}\right)_a \qquad (4)$$

and the sum of all terms must satisfy

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{1}{c_s}\sum_{i=1}^{n} D_i\left(\frac{\partial c_i}{\partial r}\right)_a \qquad (5)$$

The assumption of Henry's law means that the dissolved concentration of gas at the surface of the bubble must be

$$c_i(a) = H_i P g_i \qquad (6)$$

where H_i is the solubility at one atmosphere and P is the total pressure in the bubble in atmospheres. The other boundary and initial conditions are written as usual,

$$c_i(\infty) = c_{i\infty}; \quad t > 0 \quad \text{and}$$
$$c_i(r) = c_{i\infty}; \quad r > a, \quad t = 0 \qquad (7)$$

The following dimensionless variables were used,

$$z = \frac{D_1 t}{a_0^2} \quad f_i = \frac{D_i}{D_1} \quad R = \frac{a}{a_0}$$
$$e = \frac{r}{a_0} \quad F_i = \frac{c_i - c_{i\infty}}{c_s}$$

where a_0 is the initial radius of a bubble which grows or dissolves from finite initial size. In terms of these variables Equations 1 to 5 become

$$f_i\frac{\partial^2 F_i}{\partial e^2} + \frac{2}{e}f_i\frac{\partial F_i}{\partial e} - \left(\frac{R}{e}\right)^2\frac{\mathrm{d}R}{\mathrm{d}z}\frac{\partial F_i}{\partial e} = \frac{\partial F_i}{\partial z} \qquad (8)$$

$$\frac{\mathrm{d}g_i}{\mathrm{d}z} = \frac{3}{R}\left[f_i\left(\frac{\mathrm{d}F_i}{\mathrm{d}e}\right)_R - g_i\frac{\mathrm{d}R}{\mathrm{d}z}\right] \qquad (9)$$

and

$$\frac{\mathrm{d}R}{\mathrm{d}z} = \sum_{i=1}^{n} f_i\left(\frac{\partial F_i}{\partial e}\right)_R \qquad (10)$$

The interfacial concentration $c(a)$ is now given by

$$F_i(R) = \alpha_i g_i - F_{i0} \qquad (11)$$

if $\alpha_i = H_i P/c_s$ and $F_{i0} = c_{i\infty}/c_s$. The boundary conditions now are

$$F_i(\infty) = 0; \quad z > 0;$$
$$F_i(e) = 0; \quad e > R, \quad z = 0 \qquad (12)$$

3. Analytical solutions for growth from zero size

Analytical solutions have long been available for growth of one-component spheres from zero initial size, see Scriven [16]. Similar solutions have not been known for multi-component bubbles because of the greater complexity of the problem, especially difficulties due to variable interfacial concentrations. However we found, by numerical methods, that bubbles growing from finite initial size always approached an asymptotic regime having constant bubble composition and a linear relation between radius and square root of time. This led us to consider the possibility of deriving analytical solutions for this asymptotic regime of multi-component bubbles. How this may be done is now demonstrated.

If a bubble grows from zero size with constant composition $g_{i\infty}$, the interfacial composition in the liquid will be

$$F_i(R) = -\phi_i = \alpha_i g_{i\infty} - F_{i0} \qquad (13)$$

Thus, assuming that

$$F_i(s) = F_i(e, z) \quad \text{with} \quad s = e/(2z^{1/2}) \qquad (14)$$

which implies

$$R = 2\beta z^{1/2} \qquad (15)$$

transforms Equation 8 into

$$f_i\frac{\mathrm{d}^2 F_i}{\mathrm{d}s^2} + \frac{2}{s}f_i\frac{\mathrm{d}F_i}{\mathrm{d}s} - \frac{2\beta^3}{s^2}\frac{\mathrm{d}F_i}{\mathrm{d}s} = -2s\frac{\mathrm{d}F_i}{\mathrm{d}s} \qquad (16)$$

and Equation 10 becomes

$$2\beta = \sum_{i=1}^{n} f_i\left(\frac{\mathrm{d}F_i}{\mathrm{d}s}\right)_\beta \qquad (17)$$

Integrating Equation 16 gives

$$\frac{\mathrm{d}F_i}{\mathrm{d}s} = A_i s^{-2}\exp\left[\frac{-(s^2 + 2\beta^3/s)}{f_i}\right] \qquad (18)$$

where A_i is an integration constant.

After integrating Equation 18 and rearranging, the solubility parameter for each component is given by

$$\phi_i = A_i\,[2\beta\beta_i^2 \exp 2\beta_i^3]^{-1}\,\phi(\beta_i) \qquad (19)$$

where $\beta_i = \beta/f_i^{1/2}$. If the parameter $w = 1 - \beta/s$ is now introduced, the following equation defining $\phi(\beta_i)$

is seen to be identical to Scriven's [16] relation between growth rate and solubility,

$$\phi(\beta_i) = 2\beta_i^2 \int_0^1 \exp \beta_i^2 [1 + 2w - (1 - w)^{-2}] \, \mathrm{d}w \tag{20}$$

Asymptotic growth of a multi-component gas bubble can therefore be described in terms of the same relations as growth of a one-component bubble.

The above relations lead to the requirement that

$$\sum_{i=1}^{n} \left[\frac{\phi_i}{\phi(\beta_i)} \right] = 1 \tag{21}$$

Since $g_{i\infty}$ is independent of time Equation 9 now becomes

$$g_{i\infty} = f_i \frac{(\partial F_i / \partial e)_R}{\mathrm{d}R/\mathrm{d}z} \tag{22}$$

and the above relations lead to

$$g_{i\infty} = \frac{\phi_i}{\phi(\beta_i)} \tag{23}$$

These relations are obviously simpler if all the diffusivities are the same ($f_i = 1$, $i = 2, \ldots n$).

When evaluating values of β the condition

$$E(\beta) = \sum_{i=1}^{n} \left[\frac{F_{i0}}{\phi(\beta_i)} \left(1 - \frac{\alpha_i}{\alpha_i + \phi(\beta_i)} \right) \right] - 1 = 0 \tag{24}$$

must be satisfied and the solution for a multi-component bubble reduces to finding the value of β which satisfies Equation 24. This must be done numerically. For this purpose a set of discrete one-component solutions was used to find the values of $\phi(\beta_i)$ by polynomial interpolation and the Fibonacci method (Beveridge and Schechter [17]) employed to minimize the square of the error $[E(\beta)]^2$. This technique is easy to use because Equation 20 is a particular case of the following general equation which was solved by Scriven [16] for a large set of discrete points:

$$\phi(\beta_i, \varepsilon) = 2\beta_i^2 \times \int_0^1 \exp \{\beta_i^2 [1 + 2w\varepsilon - (1 - w)^{-2}]\} \, \mathrm{d}w. \tag{25}$$

The constant A_i can be obtained from Equation 19 and, on integrating Equation 18 from $s = \beta$ with a change of independent variable to $w = 1 - \beta/s$, the concentration distribution is given by

$$F_i(e/R) = \alpha_i g_{i\infty} - F_{i0} + 2\beta_i^2 g_{i\infty} \times \int_0^{1-R/e} \exp \beta_i^2 [1 + 2w - (1 - w)^{-2}] \mathrm{d}w \tag{26}$$

These analytical solutions demonstrate the simplicity of the asymptotic behaviour of multi-component bubbles. They also provide an excellent means of testing the accuracy of finite difference methods developed for growth from finite size, non-equilibrium initial composition of the gas in the bubble or dissolution of a bubble, for all of which analytical solution is impossible.

4. Numerical solutions

Neither dissolution nor the transient stage of growth from finite initial size can be solved analytically. A finite difference technique was therefore developed for this purpose and is described in detail by Frade [12]; this employs transformation of the space variable into $x = r/a = e/R$, rather than $x' = r/a_0$, which immobilizes the interface and automatically scales distance in terms of the size of the sphere. Algorithms were derived to deal with variable space mesh sizes with automatic readjustment of the discrete space mesh points. Equations 9 and 10 must both be solved to calculate the boundary conditions, given by Equation 11, required to solve Equation 8. Time intervals were estimated sequentially to avoid $\Delta R > 0.01R$ or $\Delta g > 0.01g$. The definition of dimensionless concentration adopted makes it possible to solve problems which involve a change in the sign of $[c_i(a) - c_{i\infty}]$. Techniques using normalized concentrations of the usual form $[c_i - c_i(a)]/[c_{i\infty} - c_i(a)]$, see for example Weinberg and Subramanian [14], fail to do so because of the discontinuities produced by a change of sign of $[c_{i\infty} - c(a)]$. The authors believe that this is the main reason for the failure of previous attempts to develop accurate general finite difference methods for the behaviour of multi-component bubbles.

Sequential adjustment of time increments permits computation of very large increases in size (up to $R = 10^5$) without requiring undue amounts of computing time and could also help to minimize errors caused by an inappropriate concentration distribution at the first time-step. As the effect of the initial transient becomes negligible long before such large sizes are achieved, growth from zero and from finite initial size become indistinguishable at large sizes.

5. Results

Many examples with up to five components have been computed and, in spite of complex initial transient stages, the compositions of multi-component bubbles always converged to equilibrium before the size had increased by a factor of ten. This fact and the excellent agreement between finite difference and analytical predictions of growth rate (β), equilibrium composition and equilibrium concentration profile is considered sufficient proof that both techniques give accurate results. Differences between analytical and numerical asymptotic growth rate constants (β) were always less than 1%. A range of examples for two component bubbles is given in Table I.

In all of those examples it was assumed that $\alpha_1 = F_{1\infty}$ and $\alpha_2 = F_{2\infty}$: the values of β' were obtained by putting pairs of computed (R, z) data for $R \geqslant 100$ into the equation $R = 2\beta z^{1/2}$. It can readily be seen that the asymptotic equilibrium composition is dependent on both relative solubilities and diffusivities of the gases concerned. It may also be noted that the sixth entry in the table gives, as it should, the same result as a one-component bubble.

Fig. 1 shows typical behaviour for a two-component bubble growing from finite initial size and non-equilibrium initial composition (pure

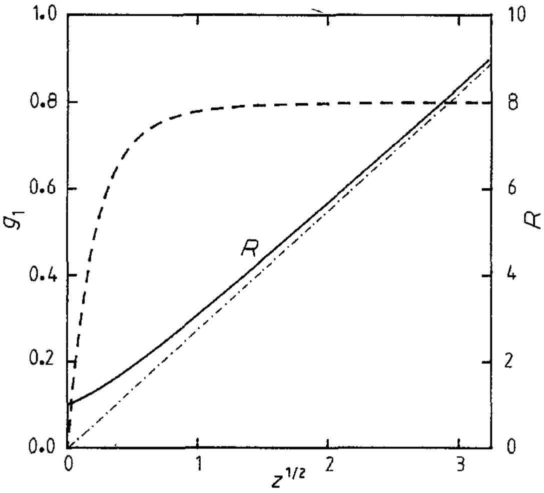

Figure 1 Transient growth of a two-component bubble from finite initial size: (——) radius, (– – –) mole fraction of Gas 1 in the bubble, (– · –) asymptotic behaviour. For Gases 1 and 2, respectively, $f_i = 1$, 0.1; $F_{i0} = 1$, 1; $\alpha_i = 0.2$, 1; $g_i(0) = 1$, 0.

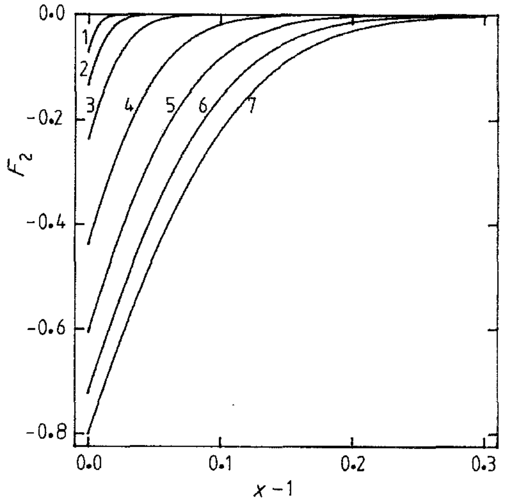

Figure 3 Concentration profiles for Gas 2 in the example shown in Fig. 1. Conditions the same as in Fig. 2. Value of R: (1) 1.025, (2) 1.05, (3) 1.1, (4) 1.25, (5) 1.5, (6) 2, (7) $\geqslant 10$.

Component 1). The composition of the bubble converges rapidly to the equilibrium value and is within 1% of that value by the time that $R = 4$; the chain line shows the analytically predicted asymptotic growth from zero size and the dashed line the change in composition. Continuing computations to $R = 10^5$ gave $g_{1\infty} = 0.8008$ and $\beta = 1.370$; the analytical solution gave the same values. Many other examples gave equally good agreement for the asymptotic behaviour and differences between β and β' generally become negligible by the time that $R = 100$.

Figs 2 and 3 show the dimensionless concentration profiles of both gases for the example shown in Fig. 1. Transient effects initially influence both the overall shapes of the concentration distributions and the interfacial concentrations but these effects have largely decayed by the time that $R = 2$. However, representation of the profile in terms of $(x - 1)$, as suggested by the analytical solution, Equation 26, makes the concentration profiles invariant for $R \geqslant 10$; these asymptotic profiles are indistinguishable from those given by Equation 26. The two concentration profiles occupy different distances because Gas 2 has ten times lower diffusivity than Gas 1. Knowing that all bubbles eventually attain an asymptotic regime having constant composition makes it easy to understand why some bubbles shrink at first and only later achieve their asymptotic growth regime. This can clearly happen if the initial bubble composition is too rich in a major mobile species; dissolution of this excess in the liquid can control the change in size during the earliest stages.

Fig. 4 shows the complex transient behaviour of a five-component bubble having a particularly interesting evolution of bubble composition. Initial shrinkage occurs here but the change in size shows quite a rapid approach to the asymptotic regime ($\beta = \beta' = 0.565$); the actual and asymptotic behaviour is almost identical for $R \geqslant 2$. Many examples have shown such initial shrinkage followed by asymptotic growth (or initial growth followed by complete dissolution). In no case has there been more than one change in the sign of $\mathrm{d}R/\mathrm{d}z$, and a sufficient range of parameters has been investigated to suggest that only one maximum or

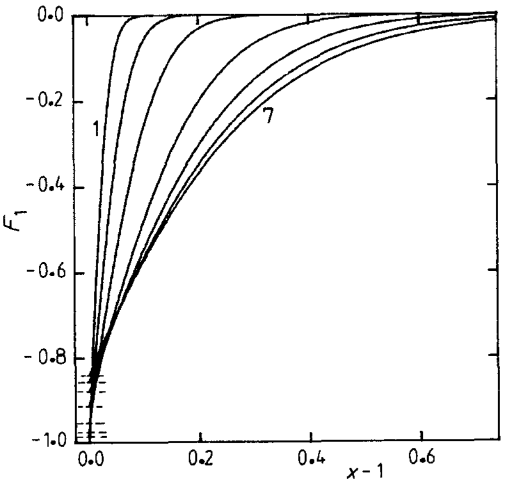

Figure 2 Concentration profiles for Gas 1 in the example shown in Fig. 1. The curves are for radii $R = 1.025$, 1.05, 1.1, 1.25, 2 and $\geqslant 10$ (from left to right). See also Fig. 3.

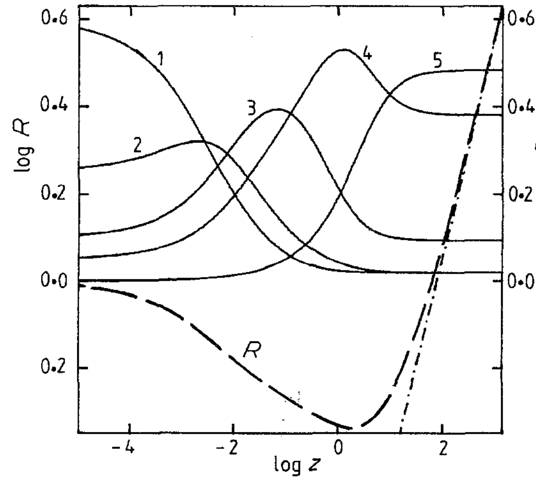

Figure 4 Transient behaviour of a five-component bubble with the parameters given in Table II. Curves labelled 1 to 5 show the proportions of each gas in the bubble; (– – –) change in size, (– · –) asymptotic growth.

TABLE I Comparison of analytical and numerical predictions for two-component bubbles in asymptotic regime

Parameters			Analytical solution		Numerical solution	
$F_{1,0}$	$F_{2,0}$	f_2	β	g_1	β'	g_1'
0.001	0.01	0.1	0.2330	0.4896	0.02333	0.4898
0.01	0.1	0.1	0.0804	0.4695	0.0804	0.4697
0.1	1.0	0.1	0.3294	0.4241	0.3297	0.4243
1.0	10.0	0.1	1.992	0.3759	1.994	0.3761
10.0	100.0	0.1	17.66	0.3619	17.67	0.3620
1.0	1.0	1.0	1.319	0.5000	1.320	0.5000
1.0	0.5	1.0	1.010	0.5858	1.011	0.5858
1.0	0.2	1.0	0.723	0.6910	0.724	0.6910
1.0	0.1	1.0	0.569	0.7697	0.569	0.7597
1.0	1.0	0.5	1.112	0.5548	1.113	0.5548
1.0	1.0	0.2	0.894	0.6250	0.894	0.6250
1.0	1.0	0.1	0.762	0.6751	0.762	0.6751

minimum is possible in any purely diffusion-controlled system.

The parameters used to produce the results shown in Fig. 4 are given in Table II. Species 1 has a relatively high solubility and diffusivity but its own equilibrium pressure in the bubble (F_{10}/α_1) would be only 0.02P. This gas therefore dissolves rapidly in the liquid until its mole fraction (g_1) is very close to 0.02 and this causes a decrease in size. Species 2 also has high solubility and low equilibrium mole fraction but a much lower diffusivity than Species 1. This gas likewise dissolves but does so more slowly than Species 1; the faster dissolution of Species 1 nevertheless causes a brief increase in the mole fraction of Species 2 before it approaches its equilibrium value which, like Species 1, is slightly below $g_i = 0.02$. Species 3 behaves much like Species 2 but the changes occur more slowly (it has lower initial mole fraction and smaller F). Species 4 by itself would have an equilibrium partial pressure of 0.5P so it diffuses into the bubble, but does so slowly because of its low diffusivity; changes in its mole fraction are, however, at first largely governed by the faster transport of Species 1, 2 and 3. Meanwhile Species 5, which was absent from the initial bubble, slowly diffuses in, increasing its mole fraction steadily, until it dilutes Species 4 and equilibrium composition is achieved soon after that. No gas showed more than one maximum or minimum in $g_i(z)$ although three of them had one extreme. Species 5 increased steadily towards its asymptotic value of $g_5 = 0.484$ and this caused Species 4 to fall from its peak of $g_4 = 0.53$ to an asymptotic value of 0.381.

Changes in the mole fraction of any gas in a bubble seem always to follow a fairly simple course with either no maximum or minimum or else only one extreme. Well defined maxima of the mole fractions, such as seen in Fig. 4, have never been predicted for bubbles which grew at all times. These maxima in composition usually require an initial decrease to minimum size before asymptotic growth is established. The last of these maxima usually occurs before the size has reached its minimum but occasionally happens at almost the same moment. Clearly defined minima are usually seen only with bubbles which dissolve completely (a subject to be dealt with in another paper) and involve gases of widely differing diffusivities. Bubbles that begin by shrinking but eventually grow seem to show the most complex evolution of gas composition, but minima in the mole fractions of any of the constituents are not typical of their behaviour. An initial decrease in size requires rapid dissolution of the major components of the original bubble. If the bubble already contains large proportions of gases which diffuse into it the changes in composition follow a much simpler pattern even if there is an initial shrinkage. Fig. 5 shows an example of this for the same gases as in Fig. 4 but the original bubble now contains 50% of Species 5, the major constituent of the equilibrium asymptotic bubble. In this case only Species 5 shows a maximum during the transient stage, its eventual decrease being attributable to the longer time necessary for Species 4 to reach its asymptotic value.

Fig. 6 shows an example of a two-component bubble which exhibits a minimum in g_1 whilst growing at all times from a composition very near to the equilibrium one. Note, however, that the scale used to show

TABLE II Parameters and conditions used for the computed results shown in Figs 4 and 5 together with the equilibrium composition of the bubble

Parameter	Component, i					Fig.
	1	2	3	4	5	
f_i	0.1	0.1	0.1	0.01	0.01	Both
F_{i0}	0.2	0.2	0.1	0.5	0.2	Both
α_i	10.0	10.0	1.0	1.0	0.1	Both
$g_i(0)$	0.6	0.25	0.10	0.05	0.0	4
	0.3	0.125	0.05	0.05	0.5	5
$g_{i\infty}'$	0.01999	0.01991	0.0954	0.3808	0.4839	(Num.)
$g_{i\infty}$	0.01999	0.01990	0.0954	0.3807	0.4840	(Anal.)

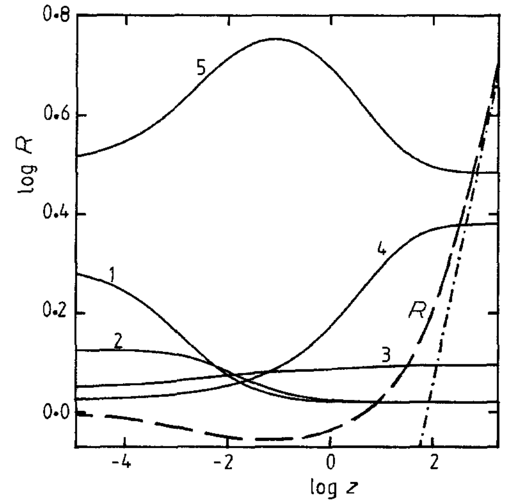

Figure 5 Transient behaviour of a five-component bubble in the same system as for Fig. 4 but this bubble initially contained 50% of Gas 5, see Table II.

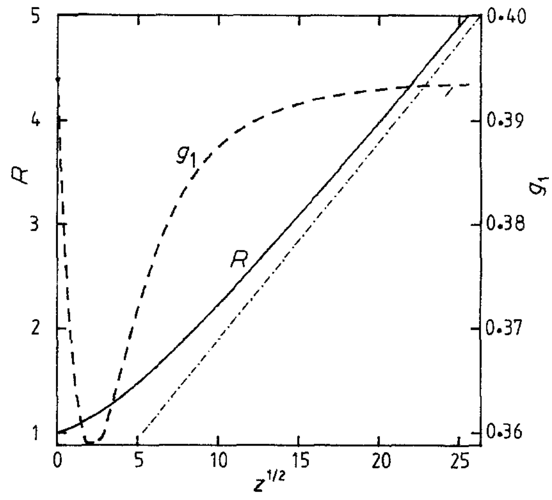

Figure 6 A two-component bubble which shows a shallow minimum in g_1 although it grows at all times: (– · –) asymptotic growth. For Gases 1 and 2, respectively, f_i = 1, 0.01; α_i = 0.01, 1; F_{i0} = 0.01, 1.

the minimum is very large and the existence of this small minimum might not be recognized in experimental data. This feature depends on the large difference in diffusivity between the two gases.

6. Conclusion

Analytical solutions show that there is an asymptotic regime for the diffusion-controlled growth of multicomponent gas bubbles in which radius varies linearly with square root of time and bubble composition is constant. This behaviour can be calculated by using the same methods as those of Scriven [16] for one-component spheres of zero initial size. Numerical methods show that the behaviour of bubbles growing from finite initial size or non-equilibrium gas composition tends quite rapidly towards this asymptotic behaviour. The excellent agreement found for rate of growth, bubble composition and concentration distributions between numerical and analytical predictions of asymptotic growth is taken to be sufficient evidence that both techniques give accurate results. It is therefore assumed that the numerical techniques developed here can be used with confidence for other problems, such as dissolving spheres, for which analytical solution is impossible.

If the initial composition of a bubble is very different from its equilibrium value it is possible for initial shrinkage to precede the eventual asymptotic growth. Changes in bubble composition can then be complex; it is possible for maxima or minima to appear in the mole fractions of the different gases present but only one extreme has been observed for any particular species. However, minima are rare and shallow where they have been seen. Maxima or minima are most likely to occur when the diffusivities of the gases concerned are very different. All the wide range of cases examined suggest that only one change of the sign of the rate of change of size is possible in any instance.

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References

1. M. CABLE, "Glass: Science and Technology", Vol. 2, Processing I (Academic Press, New York, 1984) pp. 1–44.
2. C. H. GREENE and R. F. GAFFNEY, *J. Amer. Ceram. Soc.* **42** (1959) 271.
3. C. H. GREENE and I. KITANO, *Glastechn. Ber.* **32K** (1959) V/44.
4. C. H. GREENE and H. A. LEE, *J. Amer. Ceram. Soc.* **48** (1965) 528.
5. C. H. GREENE and D. R. PLATTS, *ibid.* **52** (1969) 106.
6. M. CABLE, *Glass Technol.* **2** (1961) 60.
7. P. S. EPSTEIN and M. S. PLESSET, *J. Chem. Phys.* **18** (1950) 1505.
8. D. W. READEY and A. R. COOPER, *Chem. Engng Sci.* **21** (1966) 917.
9. M. CABLE and D. J. EVANS, *J. Appl. Phys.* **38** (1967) 2899.
10. J. L. DUDA and J. S. VRENTAS, *Amer. Inst. Chem. Engrs J.* **15** (1969) 351.
11. *Idem, Int. J. Heat Mass Transfer* **14** (1971) 395.
12. J. R. FRADE, PhD thesis, Sheffield University (1983).
13. F. KRÄMER, *Glastechn. Ber.* **52** (1979) 43.
14. M. C. WEINBERG and R. S. SUBRAMANIAN, *J. Amer. Ceram. Soc.* **63** 527.
15. C. GRIFFIN, PhD thesis, Sheffield University (1971).
16. L. E. SCRIVEN, *Chem. Engng Sci.* **10** (1959) 1.
17. G. BEVERIDGE and R. SCHECHTER, "Optimization, Theory and Practice" (McGraw-Hill, London, 1970).

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