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Oscillatory Behavior of a Gas Bubble Growing (or Collapsing) in Viscoelastic Liquids

A theoretical study was carried out to achieve a better understanding of the oscillatory behavior of a gas bubble growing (or collapsing) in a viscoelastic liquid, by taking into account both the hydrodynamic and diffusion effects. The Zaremba-DeWitt model was chosen to represent the rheological properties of the suspending medium. The finite difference method was employed to solve the governing system equations.

The computational results show that, in the case of *very fast* diffusion (i.e., constant bubble pressure), the oscillatory behavior of a bubble takes place only when the ratio of the initial pressure difference between the gas bubble and the liquid phase to the elastic modulus of the suspending medium is below a certain critical value. On the other hand, in the case of *very slow* diffusion, the oscillatory behavior of a bubble persists, regardless of the magnitude of the rheological properties of the suspending medium. Our study indicates further that the diffusivity of a gas has a profound influence on the occurrence of oscillatory behavior, that the elastic property of the suspending medium enhances oscillatory behavior while its viscosity plays the opposite role, and that even a Newtonian medium can give rise to an oscillatory pattern of bubble growth (or collapse), although it dampens out very quickly.

HEE JU YOO and CHANG DAE HAN

Department of Chemical Engineering
Polytechnic Institute of New York
Brooklyn, NY 11201

SCOPE

Today, plastics foam processing is one of the fastest growing polymer processing techniques for manufacturing the cellular products, either extruded or injection-molded. The success of plastic foam processes, however, depends largely on the ability of controlling cell size and its distribution in the final product, because the physical/mechanical properties of foamed products are very much affected by the cell structure (Frisch and Saunders, 1972). It is, therefore, very important to have a better understanding of the phenomena associated with the formation of gas bubbles and their growth in molten polymers during processing.

In the manufacture of foamed products using thermoplastic resins, two basic types of additives are available: (1) organic or inorganic compounds, often referred to as chemical blowing agents, which, after being blended with the resin, decompose on heating to give off gas which expands the molten polymer; and (2) volatile liquids, often referred to as physical blowing agents, which, after being injected into the molten polymer, vaporize at the boiling point, leaving gas cells in the resin. In the use of either type of blowing agent, the control of bubble growth in the molten polymer is of fundamental importance in obtaining cellular products of uniform cell size.

As may be surmised, the control of cell size and its distribution in foaming processing is dependent upon the following factors: (1) the physical and thermodynamic properties of the molten polymer/blowing agent mixture; (2) the rheological properties of molten polymer/blowing agent mixture; and (3) the temperature and pressure of the molten polymer/blowing agent mixture. Several researchers have carried out theoretical investigations of bubble growth (or collapse) in viscoelastic liquids (Street, 1968; Fogler and Goddard, 1970; Tanasawa and Yang, 1970; Ting, 1975; Zana and Leal, 1975) and in Newtonian liquids (Plesset and Zwick, 1954; Scriven, 1959; Barlow and Langlois, 1962; Marique and Houghton, 1962; Ruckenstein and Davis,

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1970). Of particular interest are the studies of Fogler and Goddard (1970) and Tanasawa and Yang (1970), who showed that the elasticity of the suspending medium can significantly retard the collapse of a bubble and produce prolonged oscillatory motion of a gas bubble during its collapse, by neglecting the diffusion process between the gas phase and the liquid phase.

In this article, we shall present our recent theoretical investigation of bubble growth (or collapse) at its *very early* stage, by including both the hydrodynamic and diffusion effects. The effects of the viscosity and elasticity of the suspending medium, and of the diffusion between the gas phase and the liquid phase, on the oscillatory behavior of bubble growth (or collapse) are discussed.

CONCLUSIONS AND SIGNIFICANCE

The following conclusions are drawn from the present investigation. (1) In the case of very fast diffusion between the gas bubble and the liquid medium, the oscillatory motion of a growing (or collapsing) bubble occurs when the suspending medium is viscoelastic and $|p_{g_0} - p_\infty|/G_0 <$ ca. 2.2. (2) In the case of very slow diffusion between the gas bubble and the liquid medium, the oscillatory behavior of bubble growth (or collapse) always takes place, regardless of the magnitudes of the system parameters. (3) The diffusion coefficient between the gas bubble and the liquid phase has a strong influence on the oscillatory behavior of a growing (or collapsing) bubble at the very early stage. Thus, any theoretical attempt at describing the bubble dynamics in a liquid must take into account the effect of diffusion. (4) The elasticity of the suspending medium enhances the oscillatory motion of the gas bubble, whereas the medium viscosity suppresses it. (5) In a Newtonian medium, the bubble oscillation, if any, during growth (or collapse) dampens out very quickly.

INTRODUCTION

Since the pioneering work of Rayleigh (1917), the growth/collapse of a stationary, spherical gas bubble suspended in an infinite liquid medium, either Newtonian or viscoelastic, has been the subject of considerable interest to many researchers.

Street (1968) performed a theoretical study of bubble growth in a viscoelastic medium, represented by the Oldroyd three-constant model, by considering the momentum transfer process, but neglecting a diffusion process between the gas and the liquid phase. He reports that the rate of bubble growth at its early stage is always greater in a viscoelastic medium than in a Newtonian medium of the same viscosity. However, Street (1968) seems to have overlooked the possibility of oscillatory motion occurring in a growing gas bubble at its *very* early stage of growth.

Fogler and Goddard (1970) studied theoretically the collapse of a spherical gas bubble in a large volume of an incompressible viscoelastic liquid represented by a linear Maxwell model of the integral type. Assuming that the pressure inside the gas bubble is constant during the entire collapse process neglecting the effect of diffusion between the gas and the liquid phase, they showed that the elastic property of the suspending medium can significantly retard the collapse of a gas bubble in the medium and can give rise to oscillatory behavior during its collapse, when the relaxation time of the suspending medium is moderately large compared to the Rayleigh collapse time. They showed further that oscillatory motion of the gas bubble during its collapse takes place when the ratio of the initial pressure difference between the gas and the liquid phase to the elastic modulus of the suspending medium is less than a certain critical value. Note that their analysis is valid only when the pressure inside the gas bubble remains constant during the entire collapse process.

Tanasawa and Yang (1970) also investigated the collapse of a gas bubble suspended in a viscoelastic liquid represented by the Oldroyd three-constant model. By taking into account the thermodynamic behavior of the gas phase inside the bubble, they observed that, when bubble oscillation occurs during collapse, viscous damping is less important in viscoelastic liquids than in purely viscous liquids. They observed further that a gas bubble collapses faster under adiabatic conditions than under isothermal conditions. Note that, in their analysis, diffusion between the gas and the liquid phase was neglected, by assuming that the mass of the gas bubble remains constant during the collapse process.

It is worth mentioning that because of the very short time span (about one unit of dimensionless time) used in their computations, Ting (1975) and Zana and Leal (1975) could not have detected bubble oscillation. However, the numerical computations done by Fogler and Goddard (1970) and Tanasawa and Yang (1970) were extended to about $t^* = 5$, where t^* denotes the dimensionless time. Their studies show that a bubble starts to oscillate at about $t^* = 1$.

We shall report in this paper our recent theoretical study on the oscillatory behavior of a gas bubble during the initial stage of its growth (or collapse). Emphasis was placed on investigating the effects of the diffusion of a gas dissolved in the suspending medium on its oscillatory behavior. Also discussed will be the effects of the medium elasticity and viscosity on the patterns of bubble oscillation during the growth (or collapse) process.

THEORETICAL DEVELOPMENT

Consider a stationary, spherical gas bubble growing (or collapsing) in a large body of a gas-charged viscoelastic liquid. Assuming that the gas-charged viscoelastic liquid is incompressible, and using spherical coordinates (r,θ,φ) with the origin at the center of the bubble, the velocity field of the liquid phase is given by:

$$v_r = v_r(r,t),\ v_\theta = v_\varphi = 0 \tag{1}$$

The equations of continuity and motion, respectively, may then be written as:

$$\frac{\partial}{\partial r}(r^2 v_r) = 0 \tag{2}$$

$$\rho\left(\frac{\partial v_r}{\partial t} + v_r\frac{\partial v_r}{\partial r}\right) = -\frac{\partial p}{\partial r} + \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\tau_{rr}) - \frac{(\tau_{\theta\theta} + \tau_{\varphi\varphi})}{r} \tag{3}$$

We shall choose the Zaremba-DeWitt model (Zaremba, 1903; DeWitt, 1955)

$$\underset{\approx}{\tau} + \lambda\frac{\mathcal{D}\underset{\approx}{\tau}}{\mathcal{D}t} = 2\eta_0\underset{\approx}{d} \tag{4}$$

to represent the rheological behavior of the liquid phase.

Noting that $v_r(r = R) = dR/dt = \dot{R}$, where R is the bubble radius, Eq. 2 may be rewritten as:

$$v_r = R^2\dot{R}/r^2 \tag{5}$$

Substituting Eq. 5 into Eq. 3 and integrating the resulting equation from $r = R$ to $r = \infty$, we have

$$\rho\left(R\ddot{R} + \frac{3}{2}\dot{R}^2\right) = p(R) - p(\infty) + \tau_{rr}(\infty) - \tau_{rr}(R) + 2\int_R^\infty \frac{(\tau_{rr} - \tau_{\theta\theta})}{r}dr \quad (6)$$

in which the spherical symmetry, $\tau_{\theta\theta} = \tau_{\varphi\varphi}$, is used. The expressions for the stress components, τ_{rr} and $\tau_{\theta\theta}$, may be written from Eq. 4, with the aid of Eq. 5, as

$$\tau_{rr}(y,t) = -\frac{4\eta_0}{\lambda}\int_0^t e^{(s-t)/\lambda}\left[\frac{R^2\dot{R}}{3y + R^3}\right]ds \quad (7)$$

$$\tau_{\theta\theta}(y,t) = -\frac{1}{2}\tau_{rr}(y,t) \quad (8)$$

in which y is defined as $y = (r^3 - R^3)/3$ and $\tau_{rr}(y,0) = 0$ is assumed.

The force balances at the bubble-liquid interface ($r = R$) and at the liquid boundary ($r = \infty$) may be written as:

$$-p(R) + \tau_{rr}(R) = -p_g + \frac{2\sigma}{R} \quad (9)$$

and

$$-p(\infty) + \tau_{rr}(\infty) = -p_\infty \quad (10)$$

respectively.

Substituting Eqs. 7–10 into Eq. 6, we obtain

$$\rho(R\ddot{R} + \frac{3}{2}\dot{R}^2) = p_g - \frac{2\sigma}{R} - p_\infty - \frac{12\eta_0}{\lambda}\int_0^t e^{(s-t)/\lambda}\left[\frac{R^2(s)\dot{R}(s)}{R^3(t) - R^3(s)}\right] ln\left(\frac{R(t)}{R(s)}\right)ds \quad (11)$$

Note that p_g in Eq. 11 varies with time t, and therefore we need an expression that relates p_g to bubble radius R. Such a relationship can be derived from a mass balance performed on the gas dissolved in the liquid phase, i.e., by Fick's Law of Diffusion,

$$\frac{\partial C_A}{\partial t} + v_r\frac{\partial C_A}{\partial r} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)\right] \quad (12)$$

As a gas bubble grows, the pressure inside the gas bubble, p_g, will decrease, giving rise to a concentration gradient at the bubble wall, which, in turn, affects the mass transfer process. Hence, Eqs. 11 and 12 must be solved simultaneously by using an expression that relates the solute concentration just outside the bubble wall, $C_w(t)$, to the concentration inside the gas bubble, $p_g(t)$. Let us assume that the expression sought for may be represented by Henry's Law,

$$C_A(R,t) = C_w(t) = K_p p_g(t) \quad (13)$$

The initial conditions for $R(t)$ and $C_A(r,t)$ may be written as

$$R(0) = R_0, \quad \dot{R}(0) = 0, \quad C_A(r,0) = C_0 \quad (14)$$

Note that, in Eq. 14, the initial condition, $\dot{R}(0) = 0$, is chosen arbitrarily for convenience, but nonzero values of $\dot{R}(0)$ can also be chosen. The boundary conditions for $C_A(r,t)$ are given by

$$C_A(\infty,t) = C_0 \quad (15)$$

$$\frac{d}{dt}(\rho_g R^3) = 3\rho D R^2\left(\frac{\partial C_A}{\partial r}\right)_{r=R} \quad (16)$$

Note that Eq. 16 represents the mass flux at the bubble boundary. Let us assume that ρ_g may be related to p_g by the ideal gas law,

$$\rho_g(t) = \frac{M}{R_g T}p_g(t) \quad (17)$$

Now, in order to obtain information on bubble growth (or collapse) we must solve Eqs. 11 and 12 simultaneously, with the aid of Eqs. 13–17. We have employed the moment (integral) method, introduced by Rosner and Epstein (1972), which permits us to combine Eqs. 12 and 16. After some mathematical manipulation, we obtain the following expression (Han and Yoo, 1981):

$$\frac{d}{dt}(\rho_g R^3) = \frac{6\rho^2 D(C_0 - C_w)^2 R^4}{\rho_g R^3 - \rho_{g0}R_0^3} \quad (18)$$

Note that the derivation of Eq. 18 must meet the following restriction:

$$\frac{\delta}{R} = \frac{\rho_g R^3 - \rho_{g0}R_0^3}{\rho(C_0 - C_w)R^3} \ll 1 \quad (19)$$

in which δ is the thickness of the concentration boundary layer (Rosner and Epstein, 1972).

Now, Eqs. 11 and 18 must be solved simultaneously for $R(t)$ and $\rho_g(t)$ with the aid of Eqs. 13 and 17, under the following initial conditions:

$$R(0) = R_0, \quad \dot{R}(0) = 0, \quad \rho_g(0) = \rho_{g0} \quad (20)$$

It is worth noting that, in an Newtonian medium, Eq. 11 reduces to

$$\rho\left(R\ddot{R} + \frac{3}{2}\dot{R}^2\right) = p_g - \frac{2\sigma}{R} - p_\infty - 4\eta_0\left(\frac{\dot{R}}{R}\right) \quad (21)$$

System equations, Eqs. 11 and 18, were solved numerically after they were recast into a set of difference equations (Yoo, 1980). The material constants needed for the numerical computations were based on a polystyrene-CO_2 system containing 0.2 wt % of CO_2, at 200°C, and the initial bubble radius was assumed to be 1 μm. The choice of the polystyrene-CO_2 system was made because it was used in our experimental investigation (Han and Yoo, 1981).

RESULTS AND DISCUSSION

Let us first consider two extreme cases: (1) very fast diffusion and (2) very slow diffusion. In the former case, the *pressure* inside the gas bubble may be assumed constant during the entire bubble growth (or collapse) (i.e., $p_g(t) = p_{g0}$), whereas in the latter case, the *mass* of a growing (or collapsing) bubble may be assumed constant, and yet, according to Eq. 17, the pressure inside the bubble varies inversely with the bubble volume (i.e., $p_g(t) = p_{g0}[(R_0/R(t))^3]$). In either case, the hydrodynamic equation, Eq. 11, and the diffusion equation, Equation 18, may be decoupled, and each equation may separately be solved for $R(t)$.

Case I: Very Fast Diffusion Process

Figures 1 and 2 show the theoretical predictions, obtained from the solution of Eq. 11, of bubble growth and collapse, respectively, in a viscoelastic liquid at different values of $(p_{g0} - p_\infty)/G_0$. Note that the numerical value of $\lambda = 0.9$ seconds used in our computation may be considered infinitely large compared to the time scale used in Figures 1 and 2, and thus the suspending medium can be considered purely elastic. It is seen in Figures 1 and 2 that the oscillatory motion of bubble growth or collapse takes place when the value of $(p_{g0} - p_\infty)/G_0$ (for bubble growth) or $(p_\infty - p_{g0})/G_0$ (for bubble collapse) is less than about 2.2.

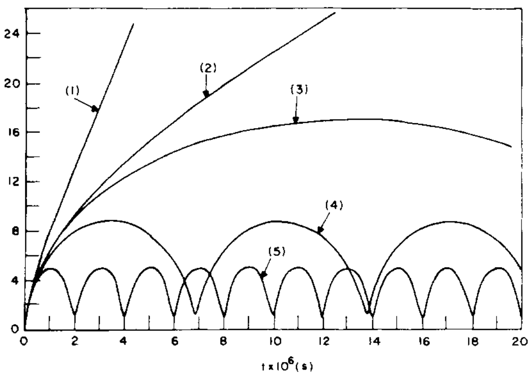

Figure 1. Bubble radius versus time during bubble growth in the case of *very fast* diffusion for different values of $(p_{g_0} - p_\infty)/G_0$: (1) 2.40; (2) 2.20; (3) 2.18; (4) 2.14; (5) 2.0. Other system parameters are : $R_0 = 1\ \mu m$; $\rho = 0.88\ g/cm^3$; $p_{g_0} = 4.693 \times 10^5\ N/m^2$; $p_\infty = 1.013 \times 10^5\ N/m^2$ (1 atm); $\sigma = 0$; $\lambda = 0.9$ s.

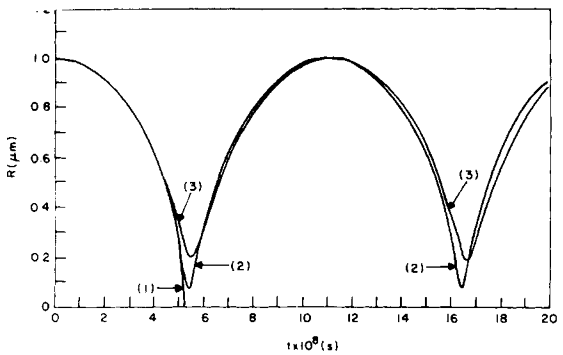

Figure 2. Bubble radius versus time during bubble collapse in the case of *very fast* diffusion for different values of $(p_\infty - p_{g_0})/G_0$: (1) 2.20; (2) 2.18; (3) 2.0. Other system parameters are the same as in Figure 1, except that $p_{g_0} = 1.013 \times 10^5$ N/m^2 and $p_\infty = 4.693 \times 10^5$ N/m^2.

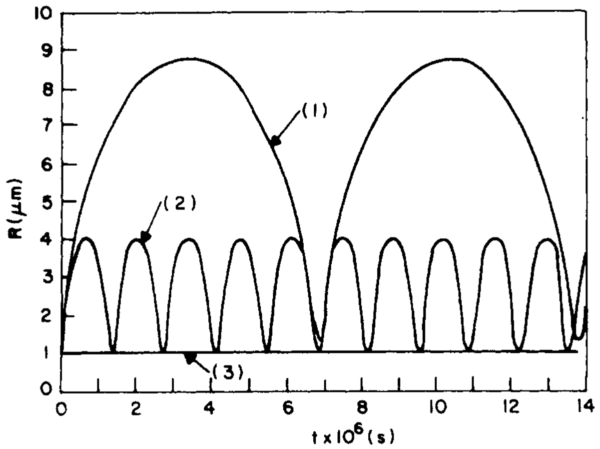

Figure 3. Bubble radius versus time during bubble growth for different values of λ: (1) 0.9 s; (2) 0.8 s; (3) 0. Other system parameters are the same as in Fig. 1, except that $\eta_0 = 1.54 \times 10^5$ N·s/m^2.

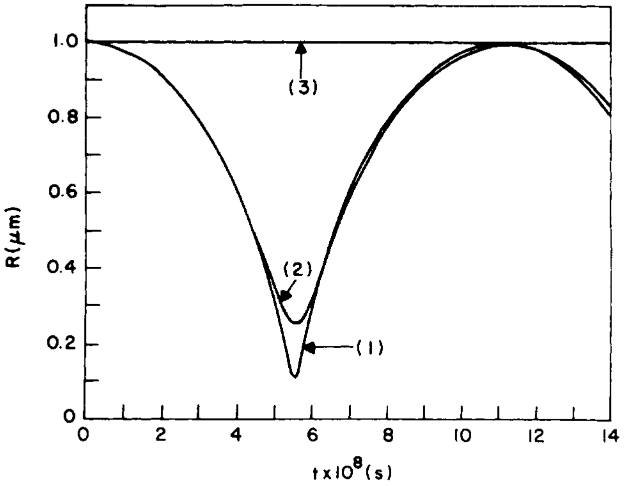

Figure 4. Bubble radius versus time during bubble collapse for different values of λ: (1) 0.9 s; (2) 0.8 s; (3) 0. Other system parameters are the same as in Fig. 2, except that $\eta_0 = 1.54 \times 10^5$ N·s/m^2.

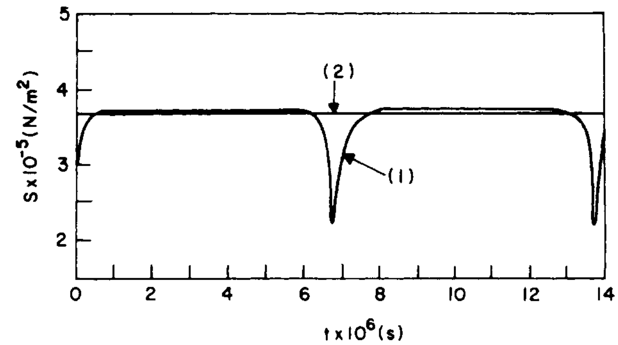

Figure 5. Stress developed in a liquid medium by the growing motion of a gas bubble: (1) in a viscoelastic medium (λ = 0.9 s); (2) in a Newtonian medium (λ = 0). Other system parameters are the same as in Figure 3.

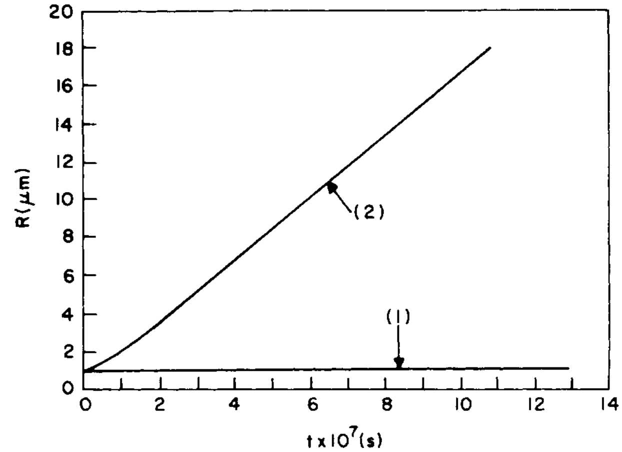

Figure 6. Bubble growth in a Newtonian medium in the case of *very fast* diffusion for different values of η_0 (N·s/m^2): (1) 4×10^3; (2) 10^{-3}. Other system parameters are the same as in Figure 1, except that $\sigma = 2.8 \times 10^{-2}$ N/m and λ = 0.

Assuming that the pressure inside the gas bubble is constant, Fogler and Goddard (1970) showed earlier from their analysis that the oscillatory behavior of a gas bubble during its collapse takes place when $(p_\infty - p_{g0})/G_0 < 2\pi^2/9$ ($\simeq 2.19$). In obtaining this criterion, they assumed that the suspending medium is a purely elastic body (i.e., the viscosity and surface tension of the suspending medium may be neglected).

Comparing the criterion for bubble oscillation obtained in the present study by a numerical method with that established by Fogler and Goddard (1970) who used an analytical method, one can find that they are in good agreement. Note that the Zaremba-DeWitt model, a rheological model of differential type, which was used in the present study, is equivalent to the one used by Fogler and Goddard, which is a linear viscoelastic model of integral type. (See Appendix.)

Figures 3 and 4 show the effect of λ on bubble oscillation during its growth and collapse, respectively. Note that curve (3) in Figures 3 and 4 represents a Newtonian liquid having the same viscosity as curve (1). Comparison of curve (1) (or curve (2)) with curve (3) leads us to conclude that the oscillation is attributable to the elastic nature of the medium.

In order to examine more closely the role of medium elasticity on bubble dynamics, let us consider the stress developed in the suspending medium due to the growing motion of the bubble, i.e., the contribution of the last term on the righthand side of Eq. 11 (for the viscoelastic medium) or Eq. 21 (for the Newtonian medium). Note that this stress depends on the rheological parameters of the suspending medium, and it acts to oppose the bubble growth. Figure 5 shows plots of this stress (S) against time (t) during the growth process of a bubble, for the cases of λ = 0.9 seconds and λ = 0 (i.e., a Newtonian fluid), which correspond to curves (1) and (3), respectively, in Figure 3. It is seen that, in the case of the viscoelastic medium (curve (1)), the stress in the medium builds up gradually as the bubble starts to grow, while in the case of the Newtonian medium (curve (2)) it remains constant. Therefore, as the stress in the viscoelastic medium builds up, the bubble growth is retarded, ultimately inducing shrinkage (i.e., collapse) of the bubble. The bubble shrinkage, in turn, slows down the build-up of the stress in the viscoelastic medium, inducing expansion (i.e., growth) of the bubble. This alternating mode of bubble expansion

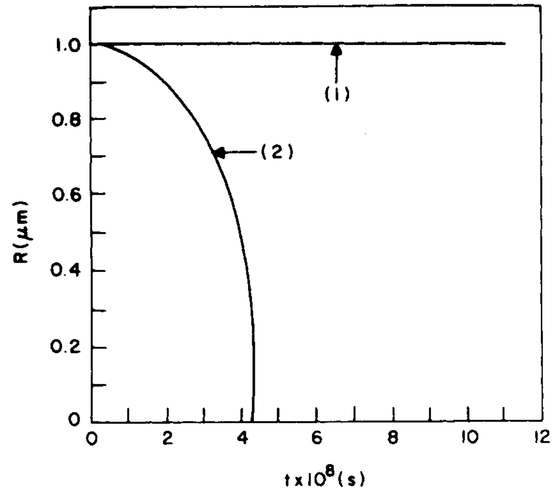

Figure 7. Bubble collapse in a Newtonian medium in the case of *very fast* diffusion for different values of η_0 (N·s/m^2): (1) 4 × 10^3; (2) 10^{-3}. Other system parameters are the same as in Figure 2, except that σ = 2.8 × 10^{-2} N/m and λ = 0.

and shrinkage is believed to be the cause of the oscillatory behavior of a gas bubble, as predicted above. (See Figures 1 to 4.)

Figures 6 and 7 show bubble growth and collapse, respectively, in a Newtonian medium, over a wide range of medium viscosities. It is seen that no bubble oscillation takes place in the Newtonian medium. It can be concluded therefore that, in the case of *very fast* diffusion, the oscillatory pattern of bubble growth (or collapse) takes place only in a viscoelastic medium.

Case II: Very Slow Diffusion Process

Note that, for the *very slow* diffusion process, the pressure inside a gas bubble, p_g, no longer remains constant, but varies with the bubble radius, R, following the relationship, $p_g/p_{g_0} = (R_0/R)^3$. This situation is somewhat similar to that considered by Tanasawa and Yang (1970), who studied bubble collapse in a viscoelastic liquid, by neglecting the diffusion process between the gas bubble and the liquid medium and by assuming that the gas inside the bubble undergoes a reversible polytropic process.

Figures 8 and 9 show some representative theoretical predictions of bubble growth and collapse, respectively, in a viscoelastic medium. It is seen that oscillatory motion of a bubble occurs for two greatly different values of $(p_{g_0} - p_\infty)/G_0$. Therefore, it can be said that, in a viscoelastic medium, bubble oscillation *always* takes place during its very early stage of growth (or collapse). This was certainly not the case when the pressure inside the bubble was assumed constant, as may be seen in Figures 1 and 2.

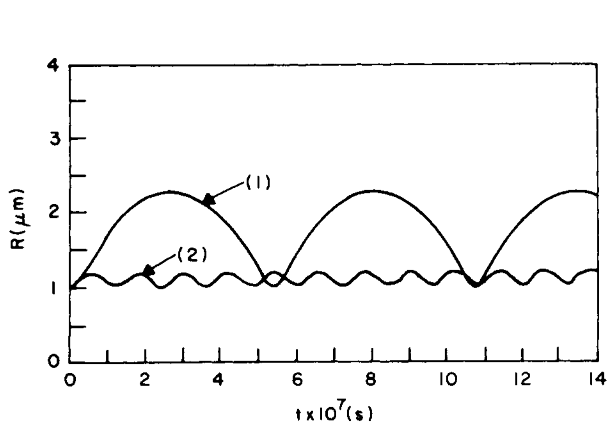

Figure 8. Bubble radius vs. time during bubble growth in the case of *very slow* diffusion for different values of $(P_{g_0} - P_\infty)/G_0$: (1) 82.8; (2) 0.6. Other system parameters are the same as in Figure 1.

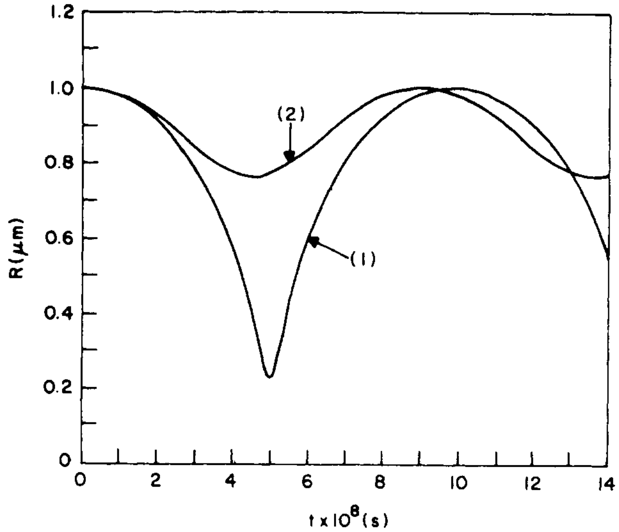

Figure 9. Bubble radius versus time during bubble collapse in the case of *very slow* diffusion for different values of $(p_\infty - p_{g_0})/G_0$: (1) 82.8; (2) 0.6. Other system parameters are the same as in Figure 2.

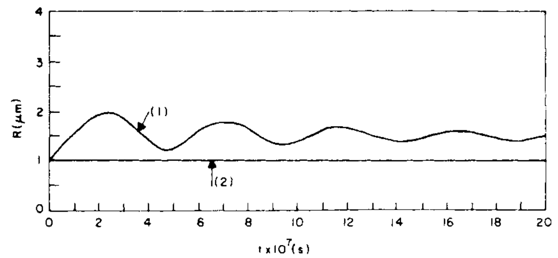

Figure 10. Bubble growth in a Newtonian medium in the case of *very slow* diffusion for different values of η_0 (N·s/m^2): (1) 10^{-3}; (2) 4 × 10^3. Other system parameters are the same as in Figure 6.

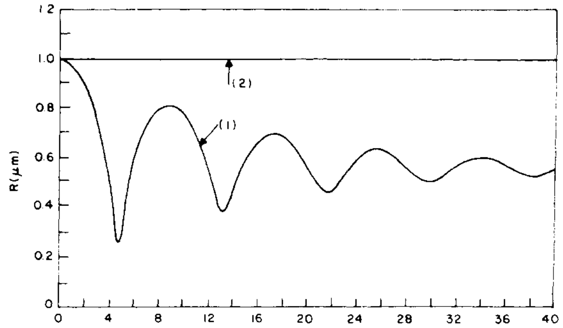

Figure 11. Bubble collapse in a Newtonian medium in the case of *very slow* diffusion for different values of η_0 (N·s/m^2): (1) 10^{-3}; (2) 4 × 10^3. Other system parameters are the same as in Figure 7.

Figures 10 and 11 show the theoretical predictions of bubble growth and collapse, respectively, in a Newtonian medium for two different values of medium viscosity. Two things are worth noting here. First, when the pressure inside the bubble does *not* remain constant, the Newtonian medium can also give rise to bubble oscillation (curve (1)), although it dampens out very quickly. Second, an increase in medium viscosity suppresses the extent of bubble oscillation. Figures 10 and 11 also show that a bubble does not grow for an indefinite period, or collapse completely, but grows (or collapses) until its equilibrium size is reached. Note that this is not true in the case of *very fast* diffusion. (See Figures 6 and 7.) In fact, in the case of *very slow* diffusion, the equilibrium bubble size can be calculated from the force balance at steady state, i.e., $p_{g0}(R_0/R_e)^3 - (2\sigma/R_e) - p_\infty = 0$, in which R_e is the equilibrium bubble size.

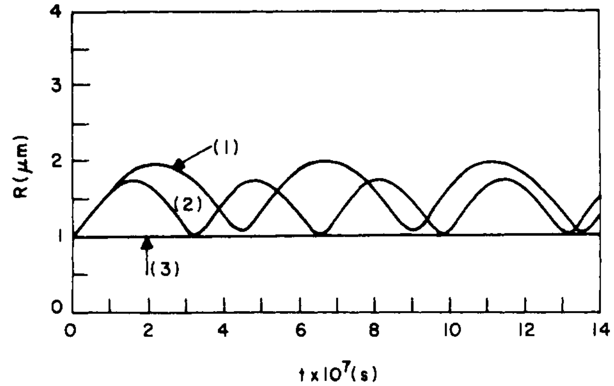

Figure 12. Bubble radius versus time during bubble growth for different values of λ: (1) 0.9 s; (2) 0.09 s; (3) 0. The value of D used is 5.5×10^{-6} cm²/s, and other system parameters are: $R_0 = 1\ \mu m$; $\rho = 0.88$ g/cm³; $p_{g_0} = 4.693 \times 10^5$ N/m²; $p_\infty = 1.013 \times 10^5$ N/m²; $\sigma = 2.8 \times 10^{-2}$ N/m; $\eta_0 = 4 \times 10^3$ N·s/m²; $K_p = 4.26 \times 10^{-9}$ m²/N.

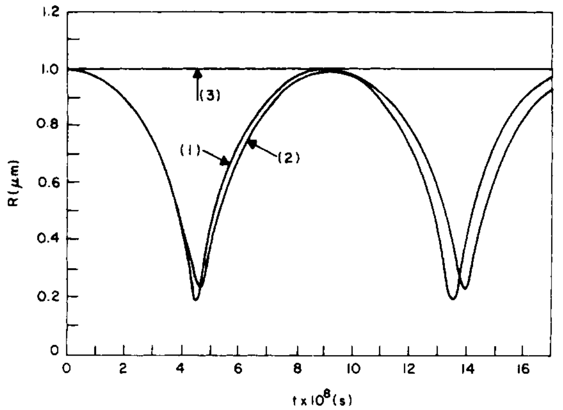

Figure 13. Bubble radius versus time during bubble collapse for different values of λ: (1) 0.9 s; (2) 0.09 s; (3) 0. The value of D used is 5.5×10^{-6} cm²/s, and other system parameters are the same as in Figure 12, except that $p_{g_0} = 1.013 \times 10^5$ N/m² and $p_\infty = 4.693 \times 10^5$ N/m².

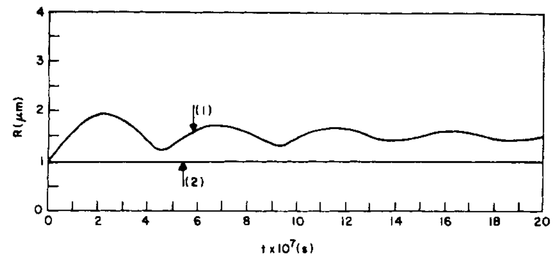

Figure 14. Bubble growth in a Newtonian medium for different values of η_0 (N·s/m²): (1) 10^{-3}; (2) 4×10^3. Other system parameters are the same as in Figure 12, except that $\lambda = 0$ and $D = 5.5 \times 10^{-6}$ cm²/s.

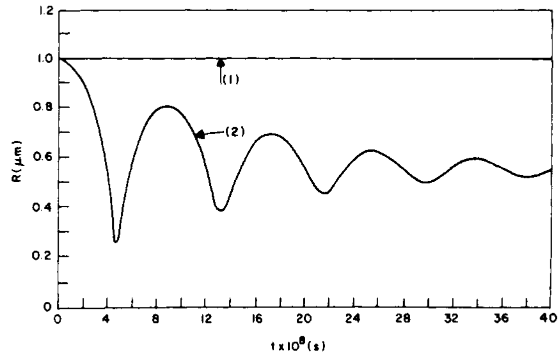

Figure 15. Bubble collapse in a Newtonian medium for different values of η_0 (N·s/m²): (1) 4×10^3; (2) 10^{-3}. Other system parameters are the same as in Figure 12, except that $\lambda = 0$ and $D = 5.5 \times 10^{-6}$ cm²/s.

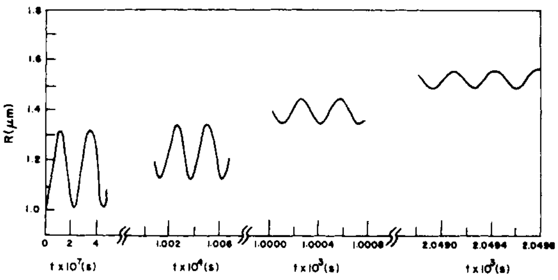

Figure 16. Oscillatory patterns of a gas bubble during its growth in a purely elastic medium. System parameters used are: $R_0 = 1\ \mu m$; $\rho = 0.88$ g/cm³; $p_{g_0} = 4.693 \times 10^5$ N/m³; $p_\infty = 2.57 \times 10^5$ N/m²; $\sigma = 2.8 \times 10^{-2}$ N/m; $\eta_0 = 4 \times 10^3$ N·s/m²; $K_p = 4.26 \times 10^{-9}$ m²/N; $\lambda \to \infty$.

For the cases shown in Figures 10 and 11, the equilibrium bubble sizes are calculated to be 1.5 μm and 0.56 μm, respectively, which is in good agreement with the asymptotic bubble sizes shown in curve (1) of Figures 10 and 11.

Case III: Intermediate Rate of Diffusion Process

Let us now consider the situation where the diffusion coefficient of a gas dissolved in the suspending medium lies in the intermediate range between the previous two extreme cases. Note that, in this situation, we must solve Eqs. 11 and 18 simultaneously. It is fair to say that any theoretical attempt at intelligently discussing the criteria for the onset of oscillatory motion of a gas bubble during its growth (or collapse) must take into account the role of the diffusion process. Note that the studies carried out by Fogler and Goddard (1970) and Tanasawa and Yang (1970) dealt only with either one of the two extreme cases, namely (1) very fast diffusion or (2) very slow diffusion.

Let us now examine the effects of the rheological properties of a gas-charged viscoelastic liquid on bubble oscillation by including the diffusion process. Note that the value of diffusion coefficient used here is based on the polystyrene-CO_2 system at 200°C. Figures 12 and 13 show the effect of λ of the suspending medium on bubble growth and collapse, respectively. It is seen that the amplitude of the oscillation increases as the value of λ is increased, suggesting that the medium elasticity enhances the oscillatory motion of a growing (or collapsing) bubble. Note in Figures 12 and 13 that the same value of viscosity ($\eta_0 = 4 \times 10^3$ N·s/m²) was used for all three cases and that *no* bubble oscillation takes place in the Newtonian medium (curve (3)). However, as shown in Figures 14 and 15, a Newtonian medium of low viscosity ($\eta_0 = 10^{-3}$ N·s/m²) gives rise to oscillatory motion at the *very beginning* although it dampens out very quickly.

So far, we have discussed the various aspects of bubble oscillation during the *very early* stage ($t < 10^{-6}$ seconds) of its growth or collapse. However, it is important for us to understand whether or not the growing (or collapsing) bubble will continue to oscillate for an indefinite period. For this, we have carried out a numerical computation of bubble growth for the period of $0 \sim 2 \times 10^{-3}$ seconds. Figure 16 shows the theoretical predictions of the oscillatory patterns of a growing bubble in a purely elastic medium. It is seen that both the amplitude and the period of oscillation decrease as the bubble continues to grow. The amplitude of oscillation is plotted against time and is given in Figure 17, in which the solid line represents the computed results and the dotted line is the extrapolation from the solid line. It is seen in Figure 17 that the amplitude decreases rather rapidly with time. Therefore, we would expect that the oscillatory behavior of a gas bubble during its growth (or collapse) will dampen out to a negligible value for $t \geq 0.1$ seconds. From the above discussion, it is concluded that the oscillatory patterns of bubble growth (or collapse) in a viscoelastic medium would become important in the *very early* stage of the growth (or collapse) process.

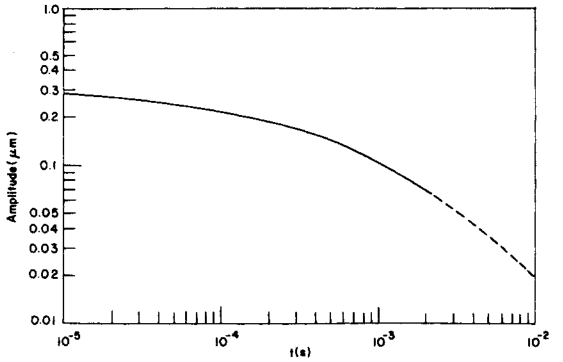

Figure 17. Amplitude of the oscillatory motion of a gas bubble versus time. System parameters are the same as in Figure 16.

We would like to draw an attention to the following points.

(1) The viscosity values used in Figures 3, 6, 7, 12 and 13 were so large that the bubble growth (or collapse) at its early stage was almost completely suppressed. This is precisely the reason why the bubble radius appears almost constant (i.e., $R(t) \cong$ constant) in these figures.

(2) Previous investigators (Barlow and Langlois, 1962; Zana and Leal, 1975) reported that different values of initial condition $\dot{R}(0)$ have negligible effects on the subsequent bubble growth (or collapse). We confirmed such observations. More specifically, $\dot{R}(t)$ reached the same value after two or three steps in our numerical computations, regardless of the values of $\dot{R}(0)$ chosen. Since the step size used was 10^{-9} s and $\dot{R}(t)$ jumped to an order of magnitude of 10^6 within two or three steps in our computations, it is not possible for us to show in Figures 3 and 5 the effects of different values of $\dot{R}(0)$.

(3) With reference to Figure 5, in the case of the Newtonian medium the value of S increased from 0 to 3.75 almost instantly (i.e., in less than $t = 5 \times 10^{-9}$ s). Such an abrupt increase of S at around $t = 0$ gives a false impression that the value of S is exactly 3.75 at $t = 0$. With the choice of time scale given in Figure 5, it is not possible for us to show a gradual increase of S for the Newtonian medium.

ACKNOWLEDGMENT

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APPENDIX

For the flow field given by Eq. 1, the r-directed normal stress, τ_{rr}, can be written from Eq. 4 as

$$\tau_{rr}(r,t) + \lambda \left[\frac{\partial \tau_{rr}(r,t)}{\partial t} + v_r \frac{\partial \tau_{rr}(r,t)}{\partial r}\right] = 2\eta_0 \frac{\partial v_r}{\partial r} \quad (22)$$

Substitution of Eq. 5 into Eq. 22 gives

$$\tau_{rr}(r,t) + \lambda \left[\frac{\partial \tau_{rr}(r,t)}{\partial t} + \frac{R^2\dot{R}}{r^2}\frac{\partial \tau_{rr}(r,t)}{\partial r}\right] = -4\eta_0 \left(\frac{R^2\dot{R}}{r^3}\right) \quad (23)$$

By using the variable defined by $y = (r^3 - R^3)/3$, Eq. 23 may be rewritten as

$$\tau_{rr}(y,t) + \lambda \frac{\partial \tau_{rr}(y,t)}{\partial t} = -4\eta_0 \left(\frac{R^2\dot{R}}{3y + R^3}\right) \quad (24)$$

The solution of Eq. 24 can be easily found as

$$\tau_{rr}(y,t) = -4 \int_0^t \frac{\eta_0}{\lambda} e^{-(t-t')/\lambda} \left[\frac{R^2(t')\dot{R}(t')}{3y + R^3(t')}\right] dt' \quad (25)$$

Using the original variables, Eq. 25 may be rewritten as

$$\tau_{rr}(r,t) = -4 \int_0^t \frac{\eta_0}{\lambda} e^{-(t-t')/\lambda} \left[\frac{R^2(t')\dot{R}(t')}{r^3 + R^3(t') - R^3(t)}\right] dt' \quad (26)$$

On the other hand, using a linear viscoelastic fluid model of the integral type, Fogler and Goddard (1970) obtained

$$\tau_{rr}(r,t) = -4 \int_0^t N(t - t') \left[\frac{R^2(t')\dot{R}(t')}{r^3 + R^3(t') - R^3(t)}\right] dt' \quad (27)$$

in which $N(t)$ is a memory function given by

$$N(t) = \mu\delta(t) + G_0 \exp(-t/\lambda) \quad (28)$$

where δ is the Kronecker delta function and μ is a constant viscosity.

Comparing Eq. 26 with Eq. 27, one can easily recognize the similarity between the two equations.

NOTATION

C_A	= weight fraction of the gas dissolved in the liquid phase
C_0	= initial concentration of the gas dissolved in the liquid phase
C_w	= solute concentration just outside the bubble wall
D	= diffusion coefficient
$\underset{=}{d}$	= rate-of-deformation tensor
$\mathcal{D}/\mathcal{D}t$	= Jaumann derivative
G_0	= elastic modulus of the liquid phase, defined by η_0/λ
K_p	= Henry's constant defined by Eq. 13
M	= molecular weight of the gas bubble
R	= bubble radius
R_e	= bubble radius at an equilibrium state
R_g	= universal gas constant
R_0	= initial bubble radius
T	= temperature
t	= time
p	= pressure
p_g	= pressure inside the gas bubble
p_∞	= pressure of the liquid phase far away from the bubble surface
v_r, v_θ, v_φ	= r-, θ-, and φ-directional velocity component, respectively, in spherical coordinates
y	= defined as $(r^3 - R^3)/3$

Greek Letters

ρ	= density of the liquid phase
ρ_g	= density of the gas inside the bubble
ρ_{g0}	= density of the gas bubble at $t = 0$
λ	= relaxation time constant of the liquid phase
η_0	= zero shear viscosity of the liquid phase
σ	= surface tension
δ	= thickness of the concentration boundary layer
$\underset{=}{\tau}$	= extra stress tensor

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Kinetics of Absorption of Carbon Dioxide into Aqueous Sodium Sulfite Solutions

The rates of absorption of pure carbon dioxide into aqueous sodium sulfite solutions containing or not containing sodium sulfate were measured at 15, 25, 35 and 45°C and at atmospheric pressure using a liquid-jet column, a wetted-wall column, and a quiescent-liquid absorber. The experimental results were analyzed by the chemical absorption theory based on the penetration model. The second-order forward rate constants for the reaction between carbon dioxide and sulfite ion in aqueous solutions were calculated and correlated as a function of temperature and ionic strength of the solution. The chemical equilibrium constants for the reaction were also determined from the measurements of the total solubility of carbon dioxide in aqueous sodium sulfite solutions.

HARUO HIKITA,
SATORU ASAI,
AKINORI YANO
and HARUJI NOSE
Department of Chemical Engineering
University of Osaka Prefecture
Sakai, Osaka, Japan

SCOPE

The simultaneous absorption of sulfur dioxide and carbon dioxide into aqueous solutions of sodium sulfite is industrially practiced as the Wellman-Load process for the removal of sulfur dioxide from flue gases. For the rational design of absorption equipment in such a process, the knowledge of the mechanism of chemical absorption for the sulfur dioxide-sodium sulfite system and the carbon dioxide-sodium sulfite system is required. In a previous paper (Hikita et al., 1977), the absorption of sulfur dioxide into aqueous sodium sulfite solutions was studied and found to be accompanied by an instantaneous irreversible reaction between the dissolved sulfur dioxide and sulfite ion in the solution.

The purpose of the study decreased in this paper is to clarify the mechanism and kinetics of chemical absorption of carbon dioxide into aqueous sodium sulfite solutions.

CONCLUSIONS AND SIGNIFICANCE

Experiments have been carried out on the absorption of pure carbon dioxide into aqueous sodium sulfite solutions containing and not containing sodium sulfate at atmospheric pressure and at 15, 25, 35 and 45°C, using a liquid-jet column, a wetted-wall column, and a quiescent-liquid absorber. The measured absorption rates were analyzed by the chemical absorption theory based on the penetration model. The values of the second-order forward rate constant for the reaction between carbon dioxide and sodium sulfite in aqueous solutions were determined from the measured absorption rates by fitting the experimental data to the theoretical equation. The calculated value of the rate constant ranged from 8.44×10^{-3} to 2.10×10^{-1} $m^3/mol \cdot s$ and was found to increase with increasing temperature and ionic strength of the solution.

The chemical equilibrium constant for the reaction between carbon dioxide and sodium sulfite was also determined by measuring the total solubility of carbon dioxide in aqueous sodium sulfite solutions at 15, 25 and 45°C by the method of Markham and Kobe (1941). The equilibrium constant varied from 2.82 to 4.80 and was found to increase with temperature and decrease slightly with an increase in the sodium ion concentration above about 200 mol/m^3.

From the observed values of the rate constant and the equilibrium constant between carbon dioxide and sodium sulfite, it can be concluded that the absorption of carbon dioxide into aqueous sodium sulfite solutions is a process of absorption accompanied by a reversible reaction with a finite reaction rate of the type $A + B \rightleftharpoons E + F$. These results, together with our previous results for the sulfur dioxide-sodium sulfite system (Hikita et al., 1977), may be used to interpret the mechanism of simultaneous absorption of sulfur dioxide and carbon dioxide into aqueous sodium sulfite solutions.