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ON THE MECHANISM OF ELECTROLYTIC GAS EVOLUTION

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ON THE MECHANISM OF ELECTROLYTIC GAS EVOLUTION

Huk Yuk Cheh
(Ph.D. Thesis)

February 1967
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ON THE MECHANISM OF ELECTROLYTIC GAS EVOLUTION

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ABSTRACT

A review on the various steps involved in the formation of a gas phase at an electrode-solution interface and on the mass transfer aspects associated with the overall process is presented. The analogies between electrolytic gas evolution and nucleate boiling are also discussed.

Theoretical calculations on the dynamics of asymptotic bubble growth in an initially nonuniform concentration or temperature field are performed. For the case of electrolytic gas evolution, a significant simplification is achieved by noting that the Jakob number for mass transfer is usually small so that the convective transport can be neglected in comparison with the diffusive transport. Numerical solutions are obtained for the growth rate of a hemispherical bubble on an electrode surface with linear and exponential initial concentration fields of the electrolytically generated gas and also for the cases involving initial concentration fields resulting from the constant potential and constant current experiments. For the case of nucleate boiling, the parametric solution of Skinner and Bankoff using the thin thermal boundary layer approximation associated with the large Jakob number for heat transfer is applied to obtain numerical solutions for the cases of constant potential and constant current.
Theoretical calculations for fluid flow and for mass transfer to rising bubbles or drops at both large Re and large Pe numbers are performed using the boundary layer approach of Levich. Satisfactory agreement is obtained when comparison is made to available experimental data.

Possible extensions for future investigations are outlined.
I. INTRODUCTION

In many important electrolytic processes the products of electrode reactions are gases. A phenomenological description of such a process includes the transport of the reacting species to the electrode, the rate of the charge transfer reaction and the separation of the product species from the electrode.

Much effort has been devoted to the investigation of the rate and the mechanism of electrochemical reactions. The hindrance of the overall process by mass transport must be quantitatively accounted for in order to gain a basic understanding of the charge transfer reaction. It has often been cited in the literature that the rate of a gas evolving reaction is controlled by the transfer of the gaseous product away from the electrode. Such a conclusion was often obtained from a qualitative rather than a quantitative consideration.

Following the charge transfer reaction, the nucleation of gas bubbles often proceeds at specific active sites on the electrode. The gas bubble will then grow towards a maximum size, and separation from the surface will result. The appearance and "liberation" of a gas phase on an electrode surface show significant similarities to the manner in which vapor bubbles evolve and propagate from heated surfaces in nucleate boiling of liquids. If the mass transport of the gas away from the electrode is the rate limiting step for the gas evolving reaction, the process of electrolytic gas evolution and that of nucleate boiling become analogous. Under such a condition, a constant wall temperature experiment in boiling corresponds to maintaining an electrode at a constant potential with respect to an equilibrium reference electrode, whereas the case of constant heat flux corresponds to the galvanostatic formation of gas
on an electrode.

The purpose of this investigation is to review the information available in the literature concerning the formation of a gas phase at a solid-liquid interface. Theoretical calculations will then be made to obtain an understanding of the mechanism of gas evolution.

II. REVIEW OF LITERATURE

The evolution of a gas phase at a solid-liquid interface consists of a series of consecutive steps. Following the charge transfer reaction and the formation of the product molecular species, the gas begins to diffuse away from the electrode. Due to the slowness of the diffusion process, the electrode-solution interface will become sufficiently supersaturated for nucleation to begin spontaneously. Nucleation will be considered as the first step for the gas generation process. Stable bubble nuclei grow continuously by evaporation. Supersaturation serves as the driving force for gas phase growth in electrolytic gas generation, whereas superheat is the driving force for vapor phase growth in nucleate boiling. If a bubble is attached to a horizontal surface facing upward, it cannot grow indefinitely. The buoyancy force will finally overcome the surface force which holds the bubble and separation from the surface will result. Additional mass transfer will occur during the rise of the bubble. A complete knowledge of these various steps would, in principle, enable us to understand the mass or heat transfer aspects of the gas generation process.

In this section we shall review the available information concerning these various steps and attempts to calculate the mass transfer coefficient for such a process.

1. The Theory of Nucleation

Nucleation is the first step for the formation of a new phase. The
nucleus, according to Volmer \(^5\), is a region of the new phase which is in equilibrium with the parent phase. Frenkel \(^6\) extended this definition to include any inhomogeneity in the homogeneous phase, not necessarily in equilibrium. In this review, we shall call the Volmer nucleus "the equilibrium nucleus" and "nucleus" according to the definition of Frenkel.

The formation of a nucleus is a result of molecular fluctuations which depend on the condition of the environment. The purpose of the theory of nucleation is to calculate the rate of formation of equilibrium nuclei in a given environment. This includes the calculation of the work which is required to form an equilibrium nucleus and a frequency factor for the rate expression.

A. The Work of Formation of an Equilibrium Nucleus

Nucleation often proceeds in constant temperature and constant chemical potential conditions. Following Uhlmann and Chalmers \(^7\), we shall use a less familiar but convenient potential, \(\Omega\), for this process. \(\Omega\) is defined by

\[
\Omega = U - TS - \sum_{i} n_i \mu_i = -PV, \quad (\text{II-1})
\]

where \(U\) is the internal energy, \(S\) is the entropy, \(n_i\) is the number of moles of species \(i\), \(\mu_i\) is the chemical potential of species \(i\), \(T\) is the temperature, \(P\) is the pressure and \(V\) is the volume. Therefore,

\[
d\Omega = -SdT - \sum_{i} n_i d\mu_i - PdV. \quad (\text{II-2})
\]

When a nucleus, \(\alpha\), is formed in the initially homogeneous phase, \(\beta\), at constant temperature and constant chemical potential, the appropriate potential for the system is

\[
\Omega = -P_{\alpha} V_{\alpha} - P_{\beta} V_{\beta} + \gamma A + \sum_{i} n_i \mu_i, \quad (\text{II-3})
\]
where \( \gamma \) is the surface tension and \( A \) is the interfacial area. The potential for the original homogeneous system is

\[
\Omega = -P \beta V + \sum_i n_i \mu_i, \tag{II-4}
\]

where \( V = V_\alpha + V_\beta \).

The work of formation of a nucleus, \( W \), is then given by the difference in \( \Omega \),

\[
W = \Delta \Omega = -(P_\alpha - P_\beta) V_\alpha + \gamma A. \tag{II-5}
\]

For a spherical nucleus, \( V_\alpha = \frac{4}{3} \pi R^3 \) and \( A = 4\pi R^2 \). Therefore,

\[
W = -\frac{4}{3} \pi R^3 (P_\alpha - P_\beta) + 4\pi R^2 \gamma. \tag{II-6}
\]

The condition for equilibrium is

\[
dW = 0, \tag{II-7}
\]

Therefore the radius of the equilibrium nucleus \( R^* \) can be obtained by letting \( \frac{dW}{dR}_{R=R^*} = 0 \) and solving for \( R^* \). The result yields the well-known Kelvin equation,

\[
P_\alpha - P_\beta = \frac{2\gamma}{R^*} \left[ 1 + \frac{R^*}{2\gamma} \frac{d\gamma}{dR} \right]. \tag{II-8}
\]

Consequently, the work of formation of an equilibrium nucleus is obtained by substituting equation (II-8) into equation (II-6):

\[
W^* = \frac{4}{3} \pi R^* \gamma \left[ 1 - \frac{R^*}{\gamma} \frac{d\gamma}{dR} \right] = \frac{\gamma V_\alpha^*}{R^*} - V_\alpha (\frac{d\gamma}{dR}). \tag{II-9}
\]

The first term in the right side of equation (II-9) was originally derived by Gibbs. The second term gives the contribution due to the dependence of surface tension on curvature; its magnitude can only be obtained from quasi-thermodynamics or statistical mechanics. Such calculations were made by Tolman, Kirkwood and Buff, Koenig, Hill.
Kondo\textsuperscript{14} and Plesner\textsuperscript{15}. For most cases the second term is small as compared to the Gibbs term. Therefore, for most practical cases equations (II-8) and (II-9) can be simplified to read

\[
P_\alpha - P_\beta = \frac{2\gamma}{R^*},
\]  

and

\[
W^* = \frac{4}{3} \pi R^* \gamma = \frac{16}{3} \pi \frac{\gamma^3}{(P_\alpha - P_\beta)^2}.
\]

For this case where temperature and chemical potential remain unchanged, the difference in pressure $P_\alpha - P_\beta$ serves as a driving force. As this driving force increases, the equilibrium radius and the work of formation of such a nucleus will decrease.

It is well-known that heterogeneous nucleation occurs more easily than homogeneous nucleation. For instance, boiling begins on heating surfaces, and crystallization begins on foreign particles (seeds). These can be understood by examining the work of formation of a new phase in equilibrium with two existing phases.

Let us examine the case of two existing phases, $\alpha$ and $\beta$, which are separated by a plane interface and a new phase, $\gamma$, which is in equilibrium with them as shown in Figure 1. For phase $\gamma$ to be in equilibrium with respect to phases $\alpha$ and $\beta$, the following condition must be satisfied,

\[
\gamma_{\alpha \gamma} \cos \theta_{\alpha \gamma} + \gamma_{\beta \gamma} \cos \theta_{\beta \gamma} = \gamma_{\alpha \beta},
\]

where $\gamma_{\alpha \gamma}$, $\gamma_{\beta \gamma}$, $\gamma_{\alpha \beta}$ are the surface tensions and $\theta_{\alpha \gamma}$, $\theta_{\beta \gamma}$, $\theta_{\alpha \beta}$ are the contact angles between phases $\alpha \gamma$, $\beta \gamma$ and $\alpha \beta$, respectively. The work of formation of phase $\gamma$ can be calculated by using the same method as that for the homogeneous case. The result is

\[
W^* = \frac{1}{3} \left( \gamma_{\alpha \gamma} A_{\alpha \gamma}^* + \gamma_{\beta \gamma} A_{\beta \gamma}^* - \gamma_{\alpha \beta} A_{\alpha \beta}^* \right) - \left[ v^*_{\alpha \gamma} \left( \frac{\partial \gamma_{\alpha \gamma}}{\partial R_{\alpha \gamma}} \right) + v^*_{\beta \gamma} \left( \frac{\partial \gamma_{\beta \gamma}}{\partial R_{\beta \gamma}} \right) \right]
\]

\[
= \frac{\gamma_{\alpha \gamma}^* A_{\alpha \gamma}}{R_{\alpha \gamma}^*} + \frac{\gamma_{\beta \gamma}^* A_{\beta \gamma}}{R_{\beta \gamma}^*} - \left[ v^*_{\alpha \gamma} \left( \frac{\partial \gamma_{\alpha \gamma}}{\partial R_{\alpha \gamma}} \right) + v^*_{\beta \gamma} \left( \frac{\partial \gamma_{\beta \gamma}}{\partial R_{\beta \gamma}} \right) \right].
\]
Figure 1. Phase $\gamma$ in Equilibrium with Phases $\alpha$ and $\beta$. 

XBL671-358
This shows clearly the analogy to the case of homogeneous nucleation. For the special case of nucleation on a wall, i.e., \( \beta \) is a solid phase, equation (II-13) reduces to

\[
W^* = \frac{\gamma_{\alpha \gamma} V^*}{R^* \alpha \gamma} - V^* \left( \frac{d\gamma_{\alpha \gamma}}{dR_{\alpha \gamma}} \right).
\] (II-14)

This equation is identical to equation (II-9). Therefore, for nuclei of same curvature and volume, the work of formation for heterogeneous nucleation is identical to the homogeneous case. However, for nuclei with the same radius of curvature but a contact angle of wetting \( \theta \) smaller than 180°, the volume of nucleus is smaller for the heterogeneous case than for homogeneous case. Consequently, the work of formation is smaller.

It must be noted here that the above derivations are based on the assumption that the nucleus is small when compared to the parent phase so that the environment such as temperature and composition remain unchanged. Methods that account for these variations have been developed by Ono and Kondo\(^{16}\), Hill\(^{17}\), Rosanov\(^{18}\) and Cahn and Hilliard\(^{19}\).

B. The Kinetics of Nucleation

A nucleus is a cluster of associated molecules. If the number of nuclei are much smaller than the number of unassociated molecules and ideal mixing between the nuclei and molecules is assumed, the equilibrium concentration of nuclei of each size follows the Boltzmann distribution. Hence, the concentration of the equilibrium nuclei \( n^*/V \) is given by

\[
\frac{n^*/V}{n/V} = \exp \left( -\frac{W^*}{kT} \right),
\] (II-15)

where \( n/V \) is the concentration of the unassociated molecules.

Assume that nuclei are formed by a series of bimolecular reactions of the form:

\[
a_i + a_1 \rightleftharpoons a_{i+1},
\] (II-16)

and

\[
a_i^* + a_1 \rightleftharpoons a_{i+1}^*,
\] (II-17)
where \( \alpha_i \) is a species consisting of \( i \) molecules.

Any nucleus whose size is larger than the equilibrium nucleus is considered to grow to a macroscopic size instantaneously and thus to be removed from the system. However, the disappearance of equilibrium nuclei is balanced by a supply of new molecules at the same rate, so that the parent phase remains in a stationary state. All the bimolecular reactions achieve equilibrium instantaneously. With these assumptions, Volmer and Weber \(^{20}\) calculated the rate of nucleation per unit volume, \( I \), in a one-component system to be

\[
I = \frac{4 \pi R^2 P n / V}{(2 \pi M k T)^{1/2}} \exp \left(-\frac{W^*/k T}{1/2}\right), \tag{II-18}
\]

where \( M \) is the molecular weight.

Becker and Döring \(^{21}\) improved Volmer and Weber's calculation by taking into account the evaporation of the new phase and the decrease of the nuclei population caused by the growth of the equilibrium nuclei to the new macroscopic phase. The concentration of the equilibrium nuclei is again considered to remain at steady state. Their result is

\[
I = I_{\text{Volmer-Weber}} \left(\frac{\tilde{V}/N}{2 \pi R^2}\right)^{1/2} \exp \left(-\frac{W^*/k T}{1/2}\right), \tag{II-19}
\]

where \( \tilde{V} \) is the molal volume of the nucleus and \( N \) is the Avogadro's number. This calculation gives a nucleation rate about two orders of magnitude smaller than the Volmer and Weber method.

For heterogeneous nucleation, the analog to equation (II-18) was derived by Dunning \(^{22}\),

\[
I = \frac{2 \pi R^2 P^2 (1 - \cos \theta)}{2 \pi M k T v_{ad}} \exp \left[-(W^* + W_{ad})/k T\right], \tag{II-20}
\]

where \( v_{ad} \) is the vibrational frequency of adsorbed molecules normal to
the surface and $W_{ad}$ is the work of adsorption.

Pound, Simnad and Yang\textsuperscript{23} calculated the nucleation rate from a surface diffusion model. The results of their analysis yield values between two to three orders of magnitude larger than Dunning's calculation.

The various theories discussed so far are all based on greatly simplified models. For instance, no surface imperfections have been considered to exist in heterogeneous nucleation, no foreign particles in homogeneous medium. These idealized systems seldom occur in practical processes. Even in model experiments it is often found that these purely physical theories predict too low a rate. Therefore, although they have very important theoretical significance, their applications to practical systems are limited. A more empirical approach would be useful. We shall review such an approach that takes into consideration surface imperfections.

C. The Effect of Surface Imperfections on Nucleation

It was observed in nucleate boiling on surfaces that the degree of superheat needed to initiate boiling depends on the nature of the surface\textsuperscript{24}. It was also found in numerous cases that hysteresis occurred in heat flux-superheat diagram depending on whether the heat flux was increasing or decreasing\textsuperscript{24}. Both phenomena can be explained qualitatively by postulating that vapor may be trapped in certain cavities on the surface. For such cavities, the whole process of nucleation is bypassed. It is, therefore, not surprising that the idealized theory of nucleation predicts too low a rate.

When a liquid is heated gradually from a subcooled temperature, few cavities are filled with vapor. Therefore, relatively high superheat is necessary to initiate boiling. The heat flux follows what a natural convection process would predict. Once boiling has started, a decrease in
temperature is often found. If, then, the liquid is cooled rapidly for a short interval and reheated, boiling will begin at a lower superheat. This demonstrates clearly the ability of cavities to retain vapor nuclei.

Higher superheat is often found to be associated with highly polished surface. A better polished surface contains smaller cavities which, due to their geometrical constriction, retain only small vapor bubbles. The relationship between the superheat and the size of a vapor bubble can easily be found by combining the Clausius-Clapeyron equation which relates the pressure difference between two phases to the temperature difference and the Kelvin equation which relates the pressure difference to the size of the bubble. The result is

\[ T - T_s = \frac{2\gamma T_s}{L\rho V}, \]  

(II-21)

where \( T_s \) is the saturation temperature of the liquid with a planar interface and \( L \) is the latent heat of vaporization. Therefore, higher superheat is necessary for small bubbles which can be retained in small cavities. A quantitative calculation, however, requires a relation between the size of a bubble to the size of the cavity in which it is trapped. Such a relation is often not available. Bankoff\(^{25}\) established criteria for the maximum size of a cavity which still possesses the ability of retaining a bubble. Hsu\(^{26}\), assuming a relation of cavity size to the size of bubbles entrapped in it, calculated the size range of active cavities in nucleate boiling. Both results agree satisfactorily with experimental observations.

There is still no accurate way of calculating the rate of formation of nuclei. The theories of nucleation established by Volmer and Weber\(^{20}\), by Becker and Döring\(^{21}\), and by Cahn and Hilliard\(^{19}\), etc., are based on rather idealized models. They provide a method of estimating the rate of
formation of nuclei which is often low as compared to those observed in practical systems. The theory that takes into consideration surface parameters succeeds in explaining a number of experimental observations but is still too qualitative to account for the formation of a macroscopic new phase on surfaces.

2. The Dynamics of Phase Growth

The growth of gas bubbles on electrodes is controlled by mass transfer with supersaturation serving as driving force, whereas the growth of vapor bubbles in nucleate boiling is controlled by heat transfer with superheat as driving force. A numerical evaluation for the dynamics of phase growth involves solving simultaneously the equation of continuity, the equation of motion and either the equation of convective diffusion for electrolytic gas evolution or the equation of heat flow for nucleate boiling. An exact solution is often too complex to be obtained. Reasonable assumptions are often used to simplify the individual problem. We shall first give the governing transport equations and then review the solutions available in the literature with special attention given to the different models and methods of simplification.

For bubbles having spherical shape in an incompressible, Newtonian fluid with no external force, the equation of continuity and the equation of motion in spherical coordinates reduce to:

\[ \frac{\partial}{\partial r} (r^2 v_r) = 0, \]  

(II-22)

and

\[ \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} = - \frac{1}{\rho_l} \frac{\partial P}{\partial r} - 2\mu \frac{\partial^2 v_r}{\partial r^2}, \]  

(II-23)

where \( r \) is the radial coordinate, \( v_r \) is the velocity in the \( r \) direction, \( t \) is the time, \( \rho_l \) is the density of the liquid and \( \mu \) is the viscosity of the liquid.
Equation (II-22) can be integrated to give
\[ v_r^2 r^2 = f(t), \] (II-24)
where \( f(t) \) can be obtained by considering a material balance across the bubble wall,
\[ \frac{d}{dt} \left[ \frac{4}{3} \pi R^3 \rho_v \right] = 4 \pi R^2 \rho_L \left[ \frac{d}{dt} v_r(R) \right], \] (II-25)
where \( R \) is the radius of the bubble. Assuming \( \rho_v \) is a constant, equation (II-25) reduces to
\[ v_r(R) R^2 = \varepsilon R^2 = f(t), \] (II-26)
where \( \varepsilon = \frac{\rho_L - \rho_v}{\rho_L} \). Combining equations (II-26) and (II-24), we obtain the following form of the equation of continuity:
\[ v_r^2 = \varepsilon R \] (II-27)
Substituting equation (II-27) into equation (II-23) and integrating over radius from the bubble surface to infinity, we obtain
\[ \frac{R R^2}{R} + (2 - \frac{1}{2} \varepsilon) R^2 + 4 \mu \frac{h}{R} = \frac{P_v + P_g - \rho_L - \frac{2Y}{\varepsilon \rho_L}}{P_v}, \] (II-28)
where \( P_v \) is the partial pressure of the vapor, \( P_g \) is the partial pressure of inert gas in the bubble and \( P_L \) is the pressure in the liquid. This is the well-known "Extended Rayleigh Equation." It demonstrates clearly the various forces involved in the dynamics of bubble growth. The first two terms in the left side represent the inertia force, the third term is the viscous force whereas the pressure and surface forces are given on the right side. This equation must be solved with the convective diffusion equation for electrolytic gas evolution,
\[ \frac{\partial c}{\partial t} + v \cdot \nabla c = D \nabla^2 c, \] (II-29)
where $c$ is the concentration of the gas and $D$ is the diffusivity, or the equation of heat flow for nucleate boiling,

$$\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T = \alpha \nabla^2 T,$$  \hspace{1cm} (II-30)

where $\alpha$ is the thermal diffusivity of the liquid. Equation (II-29) and equation (II-30) illustrate clearly the analogy between mass transfer and heat transfer.

Rayleigh integrated equation (II-28) for the case of bubbles growing in a uniformly superheated liquid by neglecting the cooling effect due to evaporation and by assuming $\epsilon=1$. The result is

$$R^2 = \left( \frac{R(0)}{R} \right) R^2(0) + \left( \frac{4Y}{3\rho L R(0)} \right) \left[ 1 - \frac{R^3(0)}{R^3} \right] - \left( \frac{2Y}{\rho L R} \right) \left[ 1 - \frac{R^2(0)}{R^2} \right],$$ \hspace{1cm} (II-31)

where $R(0) = 2Y/(\rho V(T_\infty) + P_g - P_L)$ and $T_\infty$ is the superheated liquid temperature. At the later stage of bubble growth where $R \gg R(0)$ equation (II-31) becomes

$$R^2 = \frac{4Y}{3\rho L R(0)} = \frac{2}{3\rho L} \left[ \rho V(T_\infty) + P_g - P_L \right],$$ \hspace{1cm} (II-32)

which is a constant. This result predicts too high a rate when compared to the observations made by Dergarabedian.

Epstein and Plesset calculated the growth of a gas bubble in a uniformly supersaturated solution. The problem was greatly simplified by their assumption that the diffusion layer was so thick that the convective transport can be neglected in solving equation (II-29). Thus, the problem reduces to a diffusion problem. The concentration gradient at the bubble wall is therefore,

* Unless specified, $\epsilon$ will always be taken as unity hereafter.
\[
\frac{\partial c}{\partial t} = (c_\infty - c_s) \left[ \frac{1}{R} + \frac{1}{(\pi D t)^{1/2}} \right],
\]

(II-33)

where \(c_\infty\) is the supersaturated concentration and \(c_s\) is the concentration at saturation. A material balance can now be made to relate \(\frac{d R}{dt}\) and \(\frac{\partial c}{\partial t}\). The result is

\[
\frac{d R}{d t} = \frac{D(c_\infty - c_s)}{\rho_v} \left[ \frac{1}{R} + \frac{1}{(\pi D t)^{1/2}} \right].
\]

(II-34)

The solution of \(R\) as a function of \(t\) at large \(t\) is

\[
R = \left[ \left( \frac{c_\infty - c_s}{2 \rho_v} \right)^{1/2} + \left( \frac{2 \rho_v c_\infty - c_s}{2 \rho_v} \right)^{1/2} \right] \left( \frac{2D(c_\infty - c_s)}{\rho_v t} \right)^{1/2}.
\]

(II-35)

For high degree of supersaturation where \(c_\infty - c_s \gg \rho_v\), equation (II-35) becomes

\[
R = \frac{(c_\infty - c_s)}{\rho_v} \sqrt{\frac{4Dt}{\pi}} = \frac{2}{\sqrt{\pi}} \sqrt{2Jt},
\]

(II-36)

whereas for near equilibrium where \(c_\infty - c_s \ll \rho_v\), it is,

\[
R = \sqrt{\frac{2D(c_\infty - c_s)}{\rho_v t}} = \sqrt{2Jt},
\]

(II-37)

where \(J = \frac{c_\infty - c_s}{\rho_v}\) is the Jakob number for mass transfer. This method gives reasonable results where growth is slow.

Methods that include the convective diffusion at very rapid bubble growth have been developed by Plesset and Zwick\(^{30,31}\) and also by Forster and Zuber\(^{32}\). Plesset and Zwick first solved the problem of heat diffusion across a spherical boundary with radial motion by a regular perturbation method. It was recognized that the thermal boundary layer is usually thin compared to the radius of the bubble at high superheat. Temperature varies appreciably only in the region very close to the bubble wall. The perturbation parameter they used was \(\frac{3R^3 - R^3}{3R^3}\). By retaining only terms up to the first order and neglecting the second derivative of temperature
with respect to distance, the zero-order solution was obtained by the Laplace transform method\textsuperscript{30} as

$$ T^0(R,t) = T_\infty - \left( \frac{\alpha_f}{\pi} \right)^{1/2} \int_0^t \frac{R(x)\left( \frac{\partial T}{\partial r} \right)_{r=R(x)}}{\int_0^x R'(y)dy}^{1/2} dx . \quad (\text{II-38}) $$

The first-order solution was then obtained by using the zero-order solution and by including the second derivative of temperature to be

$$ T^1(R,t) = 2\left( \frac{\alpha_f}{\pi} \right)^{1/2} \int_0^t \int_0^\xi \left[ -\left( \frac{\alpha_f}{\pi} \right)^{1/2} \int_0^\xi \frac{R^2\left( \frac{\partial T}{\partial r} \right)_{r=R(x)}}{(t-x)^{3/2}} \frac{dx}{(t-\xi)^{3/2}} \right] ^{1/2} \frac{d\xi}{R^3(\xi)}. \quad (\text{II-39}) $$

It was found that the zero-order approximation is usually sufficient to describe the temperature history. Equation (II-38) and equation (II-28) now completely determine the dynamics of bubble growth provided that the relationship between the vapor pressure and temperature is known.

For the asymptotic stage of bubble growth when the inertia, viscous and surface forces can all be neglected, the extended Rayleigh equation reduces to a trivial equation which says simply that the pressure inside the bubble is equal to that of the liquid. Under such conditions, only equation (II-38) needs to be considered. The solution of bubble growth was obtained again by Plesset and Zwick\textsuperscript{31} to be

$$ R = \sqrt{12 \frac{\kappa_f(T_\infty - T_g)}{\rho_L \alpha_f}} \sqrt{\alpha_f t} = \sqrt{\frac{12}{\pi} J \sqrt{\alpha_f t}} , \quad (\text{II-40}) $$

where $J = \frac{\kappa_f(T_\infty - T_g)}{\rho_f \alpha_f}$ is the Jakob number for heat transfer and $\kappa_f$ is the thermal conductivity of the liquid. This result illustrates clearly that the degree of superheat, $T_\infty - T_g$, serves as driving force for bubble growth.
Forster and Zuber\textsuperscript{32} considered the bubble as a spherically distributed heat sink and solved also for the dynamics of bubble growth at the asymptotic stage. Their result,

\[ R = \sqrt{\pi} J \sqrt{\alpha_k t}, \quad (\text{II-41}) \]

is 9.3\% lower than Plesset and Zwick's calculation.

The methods of Plesset and Zwick and also of Forster and Zuber are approximate in nature. However, they can be used to calculate the growth of bubble at small times. They may even be modified to apply to problems where the initial condition is not of uniform superheat or supersaturation. This is discussed in Section III.

For the initial condition of the uniform superheat or uniform supersaturation type, an exact calculation using the method of similarity transform can be performed for the case of asymptotic growth. This approach was used by Birkhoff, Margulies and Horning\textsuperscript{33} and also by Scriven\textsuperscript{34}.

The equation of heat flow for a spherically symmetric case may be written as

\[
\frac{\partial T}{\partial t} = \alpha_k \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) - \frac{\varepsilon R^2 R}{r^2} \frac{\partial T}{\partial r}. \quad (\text{II-42})
\]

The similarity variable \( S \) for this problem is found to be

\[ S = \frac{r}{2 \sqrt{\alpha_k t}} = \frac{r^\beta}{R}, \quad (\text{II-43}) \]

where \( \beta \) is the growth coefficient. The temperature and the radius of the bubble are such that

\[ T(r,t) = f(s), \quad \text{and} \quad R = 2\beta \sqrt{\alpha_k t}. \quad (\text{II-44}) \]

Equation (II-42) can now be transformed into an ordinary differential equation and solved with the appropriate boundary conditions. Birkhoff \textit{et al.}\textsuperscript{33} solved numerically the case for \( \varepsilon = 1 \) whereas Scriven\textsuperscript{34} gave the more complete solution for all \( \varepsilon \).
It is of interest to note that for large degrees of superheat or supersaturation, the exact solution reduces to the result obtained by Plesset and Zwick using a thin boundary layer approximation whereas at low degrees of superheat or supersaturation, it reduces to the result obtained by Epstein and Plesset where the convective transport is neglected. Although the method of similarity transform can be used to yield the exact solution for the case of uniform superheat, it is not usually applicable to problems where a concentration gradient or a temperature gradient exists in the solution.

Griffith\textsuperscript{35}, assuming a linear temperature distribution in the thermal boundary layer, solved numerically the growth of a hemispherical bubble attached to a horizontal heating surface. This is the first attempt to calculate the bubble growth with a nonuniform initial condition.

Skinner and Bankoff\textsuperscript{36}, using the regular perturbation approach of Plesset and Zwick, established a parametric solution for asymptotic bubble growth in general temperature fields at large superheat. The result was then applied to the cases of a linear and an exponential initial concentration field. This method provides a more realistic model of calculating bubble growth. A thorough development will be given in Section III and its results will be applied to two problems of practical interest.

3. Separation of Bubbles from Surfaces

A growing bubble cannot stay on a surface indefinitely. The buoyancy and pressure forces will eventually overcome the surface force which attaches the bubble and separation from the surface will result. We shall first present a general formulation on the stability of bubble on surfaces. Special application to bubbles formed on electrode surface will then be discussed.
A. General Formulation on the Stability of Bubbles on Surfaces

a. Equation Describing the Shape of a Bubble

Let us define the coordinate system \((x, z)\) for the bubble attached to the surface as shown in Figure 2. \(\phi\) is the angle formed by the \(z\)-axis and the normal to the gas-liquid interface and \(a\) is the radius of the base of the bubble. The Kelvin equation (equation (II-8)) for this system is

\[
P_\alpha - P_\beta = \gamma \left( \frac{\sin \phi}{x} + \frac{1}{b} \right),
\]

where \(x/\sin \phi\) and \(b\) are the two principal radii of curvature. In terms of \(x\) and \(z\), they are

\[
\frac{1}{b} = \frac{d^2 z}{dx^2} \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^{3/2}, \quad \text{and} \quad \sin \phi = \frac{dz}{dx} \left[ 1 + \left( \frac{dz}{dx} \right)^2 \right]^{-1/2}.
\]

Let \(P_{0\alpha}\) and \(P_{0\beta}\) be the pressures referring to phases \(\alpha\) and \(\beta\) at point 0. The two principal radii of curvature are equal at 0 and let each be denoted by \(b_0\). The Kelvin equation when applied to point 0 is

\[
P_{0\alpha} - P_{0\beta} = \frac{2\gamma}{b_0}.
\]

We also have the pressure difference due to gravity,

\[
P_\alpha - P_{0\alpha} = \rho_v g z,
\]

and

\[
P_\beta - P_{0\beta} = \rho_\ell g z,
\]

where \(g\) is the acceleration of gravity. Combining equations (II-45), (II-47), (II-48) and (II-49), the basic equation governing the shape of a bubble can be obtained,

\[
\frac{2}{b_0} + \frac{g z (\rho_v - \rho_\ell)}{\gamma} = \frac{\sin \phi}{x} + \frac{1}{b}.
\]

Following Bashforth and Adams\(^{37}\), who first derived this equation, let us define a dimensionless parameter
Figure 2. Schematic Diagram for a Bubble Attached to a Surface.
Equation (II-50) can be rewritten as
\[ 2 + \lambda \frac{\beta}{b_0} = - \frac{\sin \phi}{x/b_0} + \frac{1}{b/b_0} \cdot \] (II-52)

It should be noticed here that the shape of the bubble is fully characterized by \( \lambda \) whereas \( b_0 \) determines the size of the bubble at a fixed \( \lambda \).

Substituting equation (II-46) into equation (II-52), Bashforth and Adams obtained a second order differential equation governing the shape of the bubble which cannot be solved in exact form. However, numerical solution was performed and the values of \( x/z \) for \( \phi = 90^\circ \) at various \( \lambda \) and values of \( x/b_0 \) and \( z/b_0 \) for various values of \( \phi \) and \( \lambda \) were tabulated. It was clearly demonstrated from the graphical solution provided by Wark that as surface tension \( \gamma \) increases, the bubble approaches a spherical shape.

b. Equation Relating the Volume of the Bubble and the Angle of Contact

The relationship between the bubble volume and the angle of contact can be found by considering the force balance on the bubble when it is attached to the surface. The surface force that holds the bubble must be balanced by the buoyancy and pressure forces, i.e.,

\[ 2 \pi x\gamma \sin \phi = V(\rho_\beta - \rho_\gamma)g + \pi \beta(\rho_\alpha - \rho_\beta) \cdot \] (II-53)

Substituting equation (II-45) into equation (II-53) and realizing \( \phi = \pi - \theta \), equation (II-53) may be rewritten as

\[ V = \frac{\pi \gamma}{g(\rho_\beta - \rho_\gamma)} \left( \frac{1}{b} - \frac{\sin \phi}{x} \right) = \frac{\pi b_0^2 \beta^2}{\lambda} \left( \frac{1}{b} - \frac{\sin \theta}{x} \right) \cdot \] (II-54)

This equation was verified experimentally by Cox and also by Kabanov and Frumkin.
c. The Maximum Volume of a Vapor Bubble

It was shown in Wark's graphical solution\(^\text{38}\) that for each contact angle there exists a maximum volume of a bubble. The physical meaning is simply that for \(V > V_{\text{max}}\), the buoyancy and pressure forces are always greater than the surface force so that the bubble can no longer be attached to the surface. Fritz\(^\text{40}\) found that a linear relationship existed between \[
V_{\text{max}} \left( \sqrt{\frac{\gamma}{\rho V}} \right)^{1/3}
\]
and \(\theta\) for vapor bubbles in water when \(\theta < \frac{2}{3} \pi\). The result can be expressed as

\[
\left[ V_{\text{max}} \left( \sqrt{\frac{\gamma}{\rho V}} \right)^{1/3} \right]^{1/3} = \frac{3}{\pi} \theta,
\]

or

\[
\sqrt[3]{V_{\text{max}}} = \frac{3}{\pi} \theta \left[ \frac{\gamma}{g(\rho_d - \rho_s)} \right]^{1/2}.
\]

In nucleate boiling, bubbles are often spherical and small. For small contact angles when the volume loss due to the finite contact to the surface can be neglected, equation (II-56) reduces to

\[
R_{\text{max}} = 0.592 \theta \left[ \frac{\gamma}{g(\rho_d - \rho_s)} \right]^{1/2}.
\]

This equation was verified experimentally in numerous examples of nucleate boiling\(^\text{41}\).

B. Stability of Bubbles on Electrodes

Coehn and Neumann\(^\text{42}\) studied experimentally the sizes of gas bubbles on electrodes in several different electrolytes and under different current densities. Several interesting observations were claimed. For instance, in alkaline solutions, smaller bubbles separate from the cathode but larger ones at the anode whereas the reverse occurs in acid solutions. Also smaller bubbles separate from the electrode in more dilute solutions or at higher current densities. They proceeded to explain these observations
by postulating an electrostatic theory. Bubbles are charged and therefore, interact with the electrode. Electrostatic attraction between the bubbles and the electrode will make the disengagement difficult and will consequently lead to the formation of larger bubbles. Obviously, electrostatic repulsion would then be responsible for the retaining of only small bubbles on the electrode. In order to explain the influence of the electrolyte, these charges must be functions of the concentration of solution and the nature of electrolyte. Coehn and Neumann postulated an explanation but made no quantitative evaluation.

From the data on mobilities of bubbles in an electric field, Kabanov and Frumkin estimated the electrical force and compared that with the buoyancy force. For the size of bubbles observed by Coehn and Neumann, the electrostatic force is approximately six orders of magnitude smaller. This shows that whether the bubbles are charged or not, alternative explanation is necessary to account for the experimental observations.

It was shown by Möller that the contact angle of gas bubbles attached to a surface is dependent on the potential of the solution. This dependence resembles very much the electrocapillary curves of mercury. The parabolic nature of the contact angle-potential curve was confirmed by Frumkin and co-workers. Equation (II-54) gives the dependence of the volume of a bubble on the contact angle. There is not enough quantitative information about the contact angle-potential dependence to calculate the maximum size of the bubble in the experiments performed by Coehn and Neumann. However, from the parabolic nature of the contact angle-potential curve, Kabanov and Frumkin succeeded in explaining all the observations made by Coehn and Neumann.

It has been mentioned that whether the bubbles are charged or not is
not important in regard to the force balance. But there is no \textit{a priori} reason to preclude the possibility that the contact angle should depend on the charge. If there is such a dependence, then the charge on the bubble will have a definitive influence on its stability. Frumkin and Gorodetzkaya\textsuperscript{46}, in studying the kinetics of adhesion of bubbles to a mercury surface, observed an appreciable retardation in the establishment of an equilibrium contact angle in regions far from the electrocapillary maximum. It is, therefore, evident that surface charge does affect the contact angle. However, no quantitative information is yet available.

Several attempts have been made to determine the charge on bubbles. McTaggart\textsuperscript{47} and Alty\textsuperscript{48} measured the cataphoresis of gas bubbles in a horizontal cylindrical tube 5 to 6 cm in diameter, closed at both ends with metallic discs acting as electrodes. But their results are of doubtful validity due to their failure to isolate the effect of electro-osmotic flow of the electrolyte in the tube. Bach and Gilman\textsuperscript{49} tried to account for the electro-osmotic flow. However, due to experimental uncertainties, only the sign of the charge on bubbles was ascertained. It may be concluded that the problem of charge on bubbles which may play an important role in the interactions of bubbles is still largely unknown. More precise investigations are necessary to gain additional information about the stability of bubbles on surfaces.

4. Mass Transfer to Rising Bubbles

After a bubble has separated from the electrode, additional mass transfer will occur during its rise. This is a problem of general interest to many chemical engineering operations, e.g., absorption, extraction and distillation. However, theoretical calculations have, so far, only been performed for certain limiting cases. The method of approach involves
always two consecutive steps. The Navier-Stokes equation of motion is first solved for the flow field. The result is then used to compute the mass transfer coefficient. For most practical systems, the velocity of a bubble during its rise and the mass transfer to the bubble do not change significantly. A steady state calculation is therefore satisfactory.

A. Fluid Flow

For creeping motion, Stokes investigated the case of parallel flow past a solid sphere. The inertia term $\mathbf{v} \cdot \nabla \mathbf{v}$ in the equation of motion is neglected. The solutions of the velocity field are

$$v_\theta = v_\infty (1 - \frac{3}{4} \frac{R}{r} - \frac{1}{4} \frac{R^3}{r^3}) \sin \theta , \quad (II-58)$$

and

$$v_r = -v_\infty (1 - \frac{3}{2} \frac{R}{r} + \frac{1}{2} \frac{R^3}{r^3}) \cos \theta , \quad (II-59)$$

where $v_\infty$ is the velocity of rise. The well-known Stokes drag force is

$$D = 6\pi \mu v_\infty R . \quad (II-60)$$

It is important to know that no matter how slow the flow is, Stokes solution will fail at distances sufficiently far away from the sphere where the inertia term is no longer negligible.

An improvement of Stokes solution was given by Oseen, who took the inertia term partly into account by using a regular perturbation from $v_\infty$. The improved drag was found to be

$$D = 6\pi \mu v_\infty R \left(1 + \frac{3}{16} \text{Re}\right) , \quad (II-61)$$

where $\text{Re} = \frac{RV_\infty}{v}$ is the Reynolds number and $v$ is the kinematic viscosity of the fluid. Oseen's drag is applicable up to approximately $\text{Re} = 5$. However, the Oseen flow field is not valid very close to the sphere.

More recently, Proudman and Pearson applied the method of singular
perturbation between Stokes and Oseen's flow regime. They obtained one additional correction term. The result is

$$D = 6\pi \mu v_\infty R \left(1 + \frac{3}{16} \frac{\mu}{\rho} + \frac{9}{160} \frac{\mu^2}{\rho^2} \ln Re + O(Re^2)\right).$$  \hspace{1cm} (II-62)

For creeping flow past a liquid drop or a gas bubble, due to the internal circulation of the drop or the bubble phase, the velocity of rise is generally increased. By neglecting the inertia term, Hadamard and Rybczynski obtained the solution in Stokes flow regime. The velocity of rise is

$$\frac{v_\infty}{v_{\infty St}} = 3 \frac{\mu_0 + \mu_1}{2\mu_0 + 3\mu_1},$$  \hspace{1cm} (II-63)

where $v_{\infty St}$ is the Stokes velocity of rise for creeping flow past a solid sphere, $\mu_0$ is the viscosity of the outer phase and $\mu_1$ is the viscosity of the inner phase. It is obvious that $v_\infty$ approaches $v_{\infty St}$ for $\mu_1 \gg \mu_0$, which is the expected result for a solid sphere, whereas $v_\infty = 1.5 v_{\infty St}$ for $\mu_1 \ll \mu_0$, which is the result for the rise of a gas bubble in liquid.

The drag force is found to be

$$D = 6\pi \mu v_\infty \frac{2\mu_0 + 3\mu_1}{3(\mu_0 + \mu_1)}.$$  \hspace{1cm} (II-64)

The other limiting case, as opposed to creeping flow, is the potential flow where the viscous term can be neglected. The potential solutions given by Hill are

$$\begin{align*}
\bar{v}_{\theta_1} &= \frac{3}{2} v_\infty \left(1 - \frac{2r^2}{R^2}\right) \sin \theta, \\
\bar{v}_r &= \frac{3}{2} v_\infty \left(1 - \frac{1}{2} \frac{R^2}{r^2}\right) \cos \theta, \\
\bar{v}_{\theta_0} &= v_\infty \left(1 + \frac{1}{2} \frac{R^3}{r^3}\right) \sin \theta, \\
\bar{v}_r &= -v_\infty \left(1 - \frac{R^3}{r^3}\right) \cos \theta.
\end{align*}$$  \hspace{1cm} \text{for } r \leq R \text{ (inside the drop) (II-65-68)}
LeVich\textsuperscript{56} was the first one to use a boundary layer approach which may be regarded as a perturbation from the potential solution to flow past a spherical drop or bubble at high Re. However, his result is not valid because of the use of an incorrect form of the continuity equation. The boundary layer method was later adopted by Chao\textsuperscript{57}. His treatment leads to an erroneous first-order tangential velocity for flow past a bubble by a factor of $\sqrt{2}$ too small because of the neglecting of curvature terms in the equation of the radial component. The correct solution was finally obtained by Moore\textsuperscript{58}, using the boundary layer concept and the method of perturbation. The results were

$$\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1,$$  

(II-69)

where $\mathbf{v}_0$ is the potential solution given by equations (II-67) and (II-68), and $\mathbf{v}_1$ is the first order perturbation term given by

$$\mathbf{v}_{01} = -6v_\infty \left( \frac{\nu}{Rv_\infty} \right)^{1/2} \sin \theta \chi^{1/2} (\theta) f \left[ \gamma^{1/2} (\theta) \right],$$  

(II-70)

and

$$\mathbf{v}_1 = \frac{2\gamma^{1/2} (\theta)}{R \sin \theta} \left[ \frac{\gamma^{1/2} (\theta)}{2\chi^{1/2} (\theta)} \right] \int_0^\theta f(t) \, dt$$

$$+ h(\theta) \left( 2 \cot \theta - \frac{1}{3x(\theta) \sin \theta} \right) \int_0^\theta \gamma^{1/2} (\theta) \, f(t') \, dt',$$  

(II-71)

where

$$\gamma = \frac{r-R}{R} \left( \frac{Rv_\infty}{\nu} \right)^{1/2},$$  

(II-72)

$$\chi(\theta) = \frac{2}{3} \csc^4 \theta \left( \frac{2}{3} - \cos \theta + \frac{1}{3} \cos^3 \theta \right),$$  

(II-73)

$$f(t) = \text{ierfc} t = \frac{1}{\sqrt{\pi}} e^{-t^2} - \frac{2t}{\sqrt{\pi}} \int_t^\infty e^{-x^2} \, dx,$$  

(II-74)

and

$$h(\theta) = 6 \sin^2 \theta \chi^{1/2} (\theta).$$  

(II-75)
The drag was found to be
\[
D = 12 \pi \nu_\infty R \left[ 1 - 2.2 \text{Re}^{-1/2} + O(\text{Re}^{-5/6}) \right].
\]  

(II-76)

B. Mass Transfer

Most theoretical calculations have been devoted to two limiting cases - at very high or very low Peclet number. Peclet number is the product of the Reynolds and the Schmidt number. It is closely related to the thickness of the diffusion boundary layer and has the significance of a relative weighing importance of inertia momentum transport versus mass transport by diffusion. At very low Re and Pe, convective mass transport is very small when compared to diffusive transport. The limiting case is to neglect convection completely. For steady diffusion to a sphere, the result can be expressed simply by

\[
\text{Nu} = 2,
\]

(II-77)

where \( \text{Nu} = \frac{k d}{D} \) is the dimensionless mass transfer coefficient and \( k \) is the mass transfer coefficient.

Taking into consideration the convective contribution, Acrivos and Taylor\textsuperscript{59} improved equation (II-77) by using the singular perturbation method and obtained the following result which is valid at \( 0 \leq \text{Pe} \leq 1 \),

\[
\text{Nu} = 2 + \frac{1}{2} \text{Pe} + \frac{1}{4} \text{Pe}^2 \ln \text{Pe} + 0.0340 \text{Pe}^2 + \frac{1}{16} \text{Pe}^3 \ln \text{Pe}.
\]

(II-78)

At high Pe but low Re, Levich\textsuperscript{60,61} obtained solutions for both solid and fluid spheres based on a thin diffusion boundary layer approximation. For a solid sphere, the result is

\[
\text{Nu} = 1.01 \text{Pe}^{1/3},
\]

(II-79)

and

\[
\frac{\delta_N}{R} = \frac{1.60(\theta - \sin 2\theta)^{1/3}}{\sin 2\theta} \text{Pe}^{-1/3},
\]

(II-80)

where \( \delta_N \) is the thickness of the Nernst diffusion layer. It is, therefore,
justified to state that as Pe → ∞, the diffusion layer becomes very thin as compared to the radius of the sphere. The result for a fluid sphere is

\[ \text{Nu} = 0.652 \left( \frac{\mu_0}{\mu_0 + \mu_1} \right)^{1/2} \text{Pe}^{1/2}, \]  

(II-81)

and

\[ \frac{\delta_N}{R} = 2.05 \left( \frac{2 + \cos \theta}{1 + \cos \theta} \right)^{1/2} \left( \frac{\mu_0 + \mu_1}{\mu_0} \right)^{1/2} \text{Pe}^{-1/2}. \]  

(II-82)

At both high Re and Pe, only the potential solution of the fluid mechanics (cf. equations (II-65)-(II-68)) has been applied by Boussinesq to calculate the mass transfer coefficient. The result is simply

\[ \text{Nu} = 1.128 \text{Pe}^{1/2}, \]  

(II-83)

and

\[ \frac{\delta_N}{R} = 0. \]  

(II-84)

It is of interest to note here that if one replaces "the time of exposure" defined by Higbie by the time for the bubble to rise a distance equal to its diameter, then Higbie's penetration theory reduces to exactly the Boussinesq result.

There is, so far, no calculation in the literature made in the region where Moore's boundary layer flow applies. In many practical systems, the mass transfer process is carried out at moderately high Re where a boundary layer flow approach will seem to be of value. Such a calculation was performed to include both the cases of liquid drops and gas bubbles and will be given in Section IV.

5. Heat or Mass Transfer Aspects for the Overall Process

The heat or mass transfer aspects for the overall process of nucleate boiling or electrolytic gas evolution can, in principle, be quantitatively accounted for if the dynamics of each step involved in the formation of the new phase is completely understood. It is easily recognized from the
above discussions that much work is still needed to obtain this information.

In many electrochemical kinetic studies on the formation of gases on electrodes at high current densities, it was found that the mass transport of the reactant to the electrode or the product away from the electrode is often the rate limiting step. The transport of the gaseous product due to a bubble formation will be greatly enhanced. However, there is no quantitative information about such a transport process. Therefore, overpotential studies for gas evolving reactions are usually restricted to low current densities where the reaction is limited by the charge transfer step.

The use of electrolytic gas evolution as a means for stirring to improve the mass transfer rate was first investigated by Venczel and Tbl. Reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ was carried out under limiting current densities. The hydrogen gas evolution caused a very effective stirring. For a rate of $15 \text{ cm}^3 \text{ gas/cm}^2 \text{ min}$, the thickness of the Nernst diffusion layer was $0.003 \text{ mm}$ which corresponds to the smallest thickness of the diffusion layer ever observed with the most intensive stirring. The mass transfer rate was found to be approximately proportional to the square root of the gas generation rate. This was explained by using the Higbie penetration theory.

Han and Griffith attempted to calculate the heat flux-temperature relation in nucleate boiling by combining some existing information about the bubble growth and the bubble separation from the surface. Their method depends on an experimentally determined population of nucleation sites and a geometric model for bubble interactions. The results predict qualitatively the heat transfer characteristics on a superheated surface.
We have now completed our review for the various steps involved in the formation of a gas phase at a solid-liquid interface. In the next two sections theoretical calculations concerning the dynamics of bubble growth in realistic concentration or temperature fields and the mass transfer to rising bubbles or drops at high Re will be presented.

III. THE DYNAMICS OF PHASE GROWTH

Following the charge transfer reaction, the product gas species begins to diffuse away from the electrode. Due to the slowness of the diffusion process, the electrode-solution interface will become sufficiently supersaturated that bubble nuclei grow rapidly towards a macroscopic gas phase. This is a purely mass transfer controlled process.* We are interested in calculating the growth rate of such a bubble in an initially nonuniform concentration field.

1. Concentration Field Before the Appearance of a Bubble

The concentration field of a gas in a stationary electrolyte is governed by the Fick's second law of diffusion,**

\[
\frac{\partial c}{\partial t} = D \nabla^2 c. \tag{III-1}
\]

The electrode is considered planar in shape with a uniform current distribution. Equation (III-1) thus reduces to the one dimensional diffusion equation

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \tag{III-2}
\]

* Complete analogy exists between electrolytic gas evolution and nucleate boiling here. We shall use terminologies in electrolytic gas evolution with the understanding that the development in this section applies equally well to nucleate boiling. Results for the dynamics of bubble growth will be given in dimensionless form.

** Strictly speaking, it is only valid in dilute liquid solutions at constant temperature and pressure with density and diffusivity assumed to be independent of concentration.
where the coordinate $x$ is perpendicular to the electrode.

This equation will have to be solved with the appropriate boundary conditions commonly occurring in a gas evolving reaction. We shall present both the cases of a semi-infinite medium and a finite medium bounded by two parallel planes.

A. Semi-infinite Medium

a. Constant Potential

The electrode is maintained at a constant potential with respect to an equilibrium reference electrode. Since the reaction is considered to be controlled by diffusion, a constant potential experiment corresponds to maintaining the electrode-solution interface at a constant concentration $c_w$. The initial concentration of the solution is $c_\infty$. The boundary conditions are

1. at $t=0, x \geq 0$, $c = c_\infty$, \hspace{1cm} (III-3)
2. as $x \to \infty$, $t \geq 0$, $c = c_\infty$, \hspace{1cm} (III-4)
3. at $x=0, t > 0$, $c = c_w$. \hspace{1cm} (III-5)

The solution is

\[ \frac{c-c_\infty}{c_w-c_\infty} = \text{erfc} \left( \frac{x}{2 \sqrt{D} t} \right), \]

where $\text{erfc} \ z$ is the complementary error function of $z$;

\[ \text{erfc} \ z = \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-t^2} dt. \]

b. Constant Current

This corresponds to maintaining a constant rate of formation

---

* A complete analogy exists between this case and the constant wall temperature case in nucleate boiling.

** A complete analogy exists between this case and the constant heat flux case in nucleate boiling.
of gas. The boundary conditions and the solution are:

1. at \( t=0, \ x \geq 0 \), \( c=c_\infty \) \hspace{1cm} (III-7)
2. as \( x \to \infty, \ t \geq 0 \), \( c=c_\infty \) \hspace{1cm} (III-8)
3. at \( x=0, \ t > 0 \), \( D(\frac{\partial c}{\partial x}) = q \), a constant \hspace{1cm} (III-9)

and

\[
c = c_\infty + q \sqrt{\frac{4t}{D}} \operatorname{erfc} \frac{x}{2 \sqrt{Dt}} ,
\]  

(III-10)

where \( q \) is the rate of formation of gas and \( \operatorname{erfc} z \) is the integrated complementary error function:

\[
\operatorname{erfc} z = \frac{2}{\sqrt{\pi}} \int_z^\infty (t-z) e^{-t^2} dt .
\]

B. Finite Medium

a. Constant Potential

The electrolyte is bounded by two parallel planes of distance \( \ell \) apart. For this case, the boundary conditions are:

1. at \( t=0, \ 0 \leq x \leq \ell \), \( c=c_\infty \) \hspace{1cm} (III-11)
2. at \( x=0, \ t \geq 0 \), \( D(\frac{\partial c}{\partial x}) = 0 \) \hspace{1cm} (III-12)
3. at \( x=\ell, \ t > 0 \), \( c=c_\ell \) \hspace{1cm} (III-13)

The solution is:

\[
c = c_\ell + \frac{4}{\pi} \left( c_\ell - c_\infty \right) \sum_{n=0}^{\infty} \frac{(2n+1)^2 \pi^2 Dt/4 \ell^2}{(2n+1)} \cos \frac{(2n+1)\pi x}{2 \ell}
\]

(III-14)
The solution is
\[ c = c_\infty + \frac{4t}{L} + \frac{qL}{D} \left[ \frac{3x^2 - L^2}{6L^2} - \frac{2}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{n} \cdot e^{-n^2\pi^2Dt/L^2} \cos \frac{n\pi x}{L} \right] \]
\[ = c_\infty + \frac{2q(Dt)^{1/2}}{D} \sum_{n=0}^{\infty} \left[ \text{erf} \left( \frac{(2n+1)L^2 - x}{2(Dt)^{1/2}} \right) + \text{erf} \left( \frac{(2n+1)L^2 + x}{2(Dt)^{1/2}} \right) \right]. \] (III-18)

Rosebrugh and Miller reported solutions for the case where an invariant concentration at some fixed position in the cell was assumed. This condition is usually not met in processes involving gas evolution. Their results will not be elaborated here.

2. The Dynamics of Bubble Growth

When a solution is sufficiently supersaturated, spontaneous growth of nuclei into macroscopic bubbles proceeds. The solutions of the concentration field preceding the appearance of a bubble given by equations (III-6), (III-10), (III-14) and (III-18) provide us with the initial conditions for such growth in a medium where free convection is absent. The results from the case of semi-infinite media are often found to be adequate in describing the concentration field in an electrolytic cell. It is especially satisfactory when the cell is being operated at a low current density or in a cell where the electrode separation is large. The use of equations (III-14) and (III-18) which greatly complicates the mathematics does not appear to be justified here.

It was found by Plesset and Zwick, Forster and Zuber, Scriven.
and Glas and Westwater that for all practical purposes, the consideration of the asymptotic stage of growth where the viscous, the inertia and the surface forces can all be neglected in the extended Rayleigh equation is adequate for describing bubble growth. The growth of a very small bubble or nucleus is usually very slow due to the high surface force that arrests its radial motion. However, the transition from this slow growth to the asymptotic growth occurs in a very short time (approximately $10^{-2}$ sec). It is, therefore, only this later stage that provides practical interest.

For the asymptotic stage, the extended Rayleigh equation reduces to a trivial equation which states that the pressure inside the bubble is equal to the pressure in the liquid. Only the convective diffusion equation subject to the appropriate boundary conditions needs to be solved for the bubble dynamics.

A general solution for the convective diffusion equation with a general initial condition is very difficult if not impossible. Examining the physical system more closely, it is found that the gas bubble in an electrolytic process often grows at a relatively low rate, where convective transport can be neglected, whereas the vapor bubble in nucleate boiling usually grows at a sufficiently high rate where the thermal boundary layer is thin as compared to the bubble radius during most part of the bubble history. We shall now present our calculation for the dynamics of electrolytic gas evolution and also our application of Skinner and Bankoff's solution to two practical cases of interest in nucleate boiling.

A. Convective Transport Neglected

The convective diffusion equation now reduces to the diffusion
equation. The general solution for the spherically symmetric case will first be derived. The solution for the axisymmetric case will then be obtained through a transformation which reduces the axisymmetric equation to the spherically symmetric form. The general solution will then be applied to several practical problems.

a. Spherically Symmetric Case

This is the case where bubbles are assumed to be growing in a concentration field which is spherically symmetrical. In a liquid medium of infinite extent, the bubble will be spherical in shape. However, if it is attached to a surface, both the bubble and the initial concentration field must be hemispherical so that symmetry can be maintained. Figure 3 shows the hypothetical concentration field in the solution before the formation of a bubble. Figure 4 gives the schematic concentration field around the bubble during its growth.

The diffusion equation in spherical coordinates for this case is

$$\frac{\partial c}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right). \quad (\text{III-19})$$

The boundary conditions are

1. at $t=0$, $r \geq 0$, $c=f(r)$,

2. at $r=R$, $t > 0$, $c = c_s$,

3. at $r=R$, $t > 0$, a mass balance gives

$$\rho_v \frac{dV}{dt} = A \left( \frac{\partial c}{\partial r} \right)_{r=R}, \quad (\text{III-22})$$

or

$$\rho_v \frac{dR}{dt} = D \left( \frac{\partial c}{\partial r} \right)_{r=R}, \quad (\text{III-23})^*$$

where $c_s$ is the saturation concentration and $A$ is the instantaneous surface area of the bubble.

The solution to equation (III-19) subjected to boundary conditions, *Here, we have assumed that $\rho \gg c_s$. 
Figure 3a. Initial Concentration Field for the Spherically Symmetric Case.
Surface of constant concentration

Bubble

Electrode surface

Figure 4a.

Schematic Diagram for the Concentration Field for the Spherically Symmetric Case.

Figure 4b.

XBL671-361
equations (III-20) and (III-21), is
\[
c = \frac{1}{2r \sqrt{\pi Dt}} \int_{R}^{\infty} r' f(r') \left[ e^{-(r-r')^2/4Dt} e^{-(r+2R)^2/4Dt} \right] dr'
\]
\[
+ c_s \frac{R}{r} \text{erf} \frac{r-R}{2 \sqrt{Dt}} .
\]
Differentiating equation (III-24) with respect to \( r \) and letting \( r=R \), combining with equation (III-23), we obtain an integro-differential equation for the bubble history,
\[
\rho_v \frac{dR}{dt} = D \left[ \frac{1}{2r \sqrt{\pi Dt}} \int_{R}^{\infty} r' f(r') \left( \frac{r'-R}{Dt} \right) e^{-(r'-R)^2/4Dt} dr' - c_s \left( \frac{3}{R} + \frac{1}{\sqrt{\pi Dt}} \right) \right]
\]
This can be nondimensionalized by letting
\[
m = \frac{r-R}{R}, \quad \mathcal{R} = \frac{R}{L}, \quad \tau = \frac{Dt}{L^2} \quad \text{and} \quad g(m) = \frac{f(m)-c_s}{f(0)-c_s},
\]
to give a more convenient form
\[
\frac{d\mathcal{R}}{d\tau} = \frac{J}{2 \mathcal{R} \sqrt{\pi \tau}} \int_{0}^{\infty} (m+\mathcal{R}) g(m) m e^{-m^2/4\tau} \, dm,
\]
where \( J = \frac{[f(0)-c_s]}{\rho_v} \) is the Jakob number.

b. Axisymmetric Case

The spherically symmetric case in the presence of a planar electrode is a hypothetical one. The concentration field is usually of axisymmetric nature. Using spherical coordinates, this means there is no dependence on \( \phi \). Figure 5 shows the initial concentration field and Figure 6 is a schematic picture of the concentration field during the bubble growth.

The diffusion equation for this case is
Figure 5a.

Initial Concentration Field for the Axisymmetric Case (axisymmetric with respect to x-axis)
Schematic Diagram for the Concentration Field for the Axisymmetric Case (axisymmetric with respect to x-axis).
\[
\frac{\partial c}{\partial t} = D \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) \right].
\]

(III-28)

The boundary conditions are

1. at \( t=0, r \geq 0 \), \( c = f(r, \theta) \),

(III-29)

2. at \( r=R, t > 0 \), \( c = c_s \),

(III-30)

3. at \( r=R, t > 0 \), \( \rho_v \frac{dR}{dt} = \frac{D}{2} \int_0^\pi \left( \frac{\partial c}{\partial r} \right)_{r=R} \sin \theta \, d\theta \).

(III-31)

This set of equations can be transformed to the same form as that of the spherically symmetric case by letting

\[
U(r,t) = \frac{\pi}{\int_0^\pi \left[ c(r,\theta,t) - c_s \right] \sin \theta \, d\theta}
\]

\[
= \frac{\int_0^\pi \left[ f(0,\theta) - c_s \right] \sin \theta \, d\theta}{\int_0^\pi \left[ f(0,\theta) - c_s \right] \sin \theta \, d\theta}.
\]

(III-32)

In terms of \( U \), equations (III-28) to (III-31) are

\[
\frac{\partial U}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial U}{\partial r} \right),
\]

(III-33)

\[
\int_0^\pi \left[ f(r,\theta) - c_s \right] \sin \theta \, d\theta
\]

and

1. at \( t=0, r \geq 0 \), \( U = \frac{\pi}{\int_0^\pi \left[ f(0,\theta) - c_s \right] \sin \theta \, d\theta} = f'(r) \),

(III-34)

2. at \( r=R, t > 0 \), \( U = 0 \),

(III-35)

3. at \( r=R, t > 0 \), \( \rho_v \frac{dR}{dt} = \frac{D}{2} \frac{\partial U}{\partial r} \bigg|_{r=R} \).

(III-36)

Comparing equations (III-19) and (III-20, 21, 23) to equations (III-33) and (III-34, 35, 36), it is obvious that equation (III-27) is also valid for the axisymmetric case provided \( g(m) \) and \( J \) are redefined as
The radius-time history for the bubble may be obtained for various cases by solving equation (III-27) with the appropriate initial conditions \( g(m) \). An exact solution will be presented for the case of uniform initial supersaturation. For cases of general initial conditions, no exact solution can be obtained. The solution for cases of low and high Jakob numbers will then be given.

(i) Uniform Supersaturation

\[ g(m) \text{ for this case is simply unity. Equation (III-27) is, therefore,} \]

\[ \frac{dR}{d\tau} = \frac{1}{2R \sqrt{4\pi}} \int_0^\infty (m+R)me^{-m^2/4\tau} \, dm = J \left[ \frac{1}{R} + \frac{1}{\sqrt{4\tau}} \right]. \quad (III-39) \]

If we let \( \xi^2 = 2J\tau \), and \( \bar{J} = (J/2\pi)^{1/2} \), equation (III-39) simplifies to

\[ \frac{dR}{d\xi} = \frac{1}{\xi} + 2\bar{J}. \quad (III-40) \]

If the degree of supersaturation is low, \( 2\bar{J} \) will be much smaller than \( 1/R \). This is equivalent to saying that \( \int_0^\infty m^2e^{-m^2/4\tau} \, dm \) is much larger than \( \int_0^\infty \xi me^{-m^2/4\tau} \, dm \). The solution is then simply

\[ R = (2J\tau)^{1/2}, \quad (III-41) \]
or
\[ R = \sqrt{\frac{2D(c_\infty - c_s)}{\rho_v}} t. \]  

(III-42)

If the degree of supersaturation is very high, i.e., \( \frac{1}{\mathcal{C}} \) is much larger than \( \frac{1}{\mathcal{C}} \) or \( \int_0^\infty m^2 e^{-m^2/4\tau} dm \) is much smaller than \( \int_0^\infty me^{-m^2/4\tau} dm \), the solution is
\[ R = \frac{2}{\sqrt{\pi}} \tau \frac{1}{2}, \]  

(III-43)

or
\[ R = \frac{2}{\sqrt{\pi}} \frac{(c_\infty - c_s)}{\rho_v} \sqrt{Dt}. \]  

(III-44)

Equations (III-42) and (III-44) are the same as those calculated by Epstein and Plesset. A complete solution to equation (III-40) has also been obtained by them. Their result can be expressed as
\[ \xi = e^{\frac{1}{2}} \left[ \cosh((1+\xi^2)^{1/2}z) + \xi (1+\xi^2)^{-1/2} \sinh((1+\xi^2)^{1/2}z) \right], \]  

(III-45)

\[ \xi = e^{\frac{1}{2}} (1+\xi^2)^{-1/2} \sinh((1+\xi^2)^{1/2}z). \]  

(III-46)

(11) Low Supersaturation

This is the case where in equation (III-27), \( \int_0^\infty m^2 g(m)e^{-m^2/4\tau} dm \) is much larger than \( \int_0^\infty \mathcal{C}mg(m)e^{-m^2/4\tau} dm \), Equation (III-27), therefore, reduces to
\[ \frac{d\mathcal{L}}{d\tau} = \frac{J}{2\mathcal{L} \sqrt{\pi \tau}} \int_0^\infty m^2 g(m)e^{-m^2/4\tau} dm, \]  

(III-47)

which can be integrated to give
\[ \mathcal{L}^2 = 2J \int_0^\infty mg(m) \text{erfc} \frac{m}{2\tau^{1/2}} dm \cdot \]  

(III-48)

This is the basic solution for the low supersaturation case. It will now be applied to several practical cases.
(1) **Linear Concentration Field**

A linear decay of concentration from the electrode surface to the distance \( \ell \) and constant thereafter has often been used in literature in performing mass transfer calculations. This distribution can be given in spherical coordinates by

\[
f(r, \theta) = \begin{cases} 
  c_\infty + (c_w - c_\infty) (1 - \frac{r \cos \theta}{\ell}) , & r/\ell < 1, \\
  c_\infty , & 0 < \theta < \cos^{-1} \frac{\ell}{r}, \\
  c_\infty + (c_w - c_\infty) \frac{r \cos \theta}{\ell} \cos^{-1} \frac{\ell}{r} < \theta < \frac{\pi}{2}, 
\end{cases}
\]

where \( c_\infty \) is the bulk concentration and \( c_w \) is the concentration at \( \theta = \pi/2 \).

Substituting equations (III-49-51) into equation (III-37) yields

\[
g(m) = \begin{cases} 
  1 - \omega (1 - \frac{1}{2m}) , & m > 1, \\
  1 - \frac{\omega m}{2} , & m < 1, 
\end{cases}
\]

where \( \omega = \frac{c_w - c_\infty}{c_w - c_s} \).

Substituting equations (III-52) and (III-53) into equation (III-48) and integrating, the following analytic solution is obtained,

\[
\mathcal{Q}^2 = 2J \left[ \int_0^1 m (1 - \frac{\omega m}{2}) \text{erfc} \left( \frac{m}{2\tau^{1/2}} \right) dm - \int_1^\infty (1 - \omega (1 - \frac{1}{2m})) m \text{erfc} \left( \frac{m}{2\tau^{1/2}} \right) dm \right]
\]

\[
= 2J \left[ -\omega \left[ \frac{1}{6} \text{erfc} \left( \frac{1}{2\tau^{1/2}} \right) + \tau \text{erfc} \left( \frac{1}{2\tau^{1/2}} \right) + \frac{4\tau^{3/2}}{3 \sqrt{\pi}} (1 - (1 + \frac{1}{4\tau}) e^{-\frac{1}{4\tau}}) \right] \right].
\]

---

* \( \omega \) will again appear in later cases. It can be expressed more generally by

\[\omega = \frac{\text{interface concentration} - \text{bulk concentration}}{\text{interface concentration} - \text{saturation concentration}}.\]

Therefore, \( \omega = 0 \) signifies the uniform supersaturation case. \( 0 < \omega < 1 \) means that the solution is supersaturated, however a gradient of concentration from the bulk to the interface exists. \( \omega = 1 \) means the bulk solution is saturated and \( \omega > 1 \) is the case where the bulk is below saturation.
This result is given in Figures 7 and 8. For cases where \( \omega > 1 \), a maximum of radius occurs. The growth of bubble is followed by a collapse which is due to the low concentration of gas in the bulk solution.

(2) Exponential Concentration Field

A better approximation to the linear concentration field in the boundary layer is the exponential representation, i.e.,

\[
f(r, \theta) = c_\infty + (c_w - c_\infty) \exp \left( \frac{r \cos \theta}{\ell} \right), \quad 0 < \theta < \frac{\pi}{2},
\]

or

\[
g(m) = 1 - \omega \left[ 1 - \frac{1}{m} (1 - e^{-m}) \right], \quad (\text{III-57})
\]

where \( \omega = \frac{c_w - c_\infty}{c_w - c_\infty} \). Equation (III-48) can also be integrated in closed form for this case,

\[
\ell^2 = 2J \int_0^\infty \left[ m (1 - \omega) (1 - \frac{1}{m} (1 - e^{-m})) \right] \text{erfc} \frac{m}{2\sqrt{\tau}} \, dm
\]

\[
= 2J \left[ \tau \omega (\tau - \frac{2}{\sqrt{\pi}} \tau^{1/2} - 1 - e^{-\tau} \text{erfc} \frac{\tau}{2}) \right]. \quad (\text{III-58})
\]

A numerical solution is given in Figures 9 and 10.

(3) Constant Potential

The solution of the diffusion equation prior to the appearance of a bubble given by equation (III-6) provides us the initial condition for this case,

\[
f(r, \theta) = c_\infty + (c_w - c_\infty) \text{erfc} \frac{r \cos \theta}{2\sqrt{Dt}}, \quad 0 < \theta < \frac{\pi}{2},
\]

\[
= c_\infty + (c_w - c_\infty) \text{erfc} \frac{r \cos \theta}{\ell}, \quad (\text{III-59})
\]

where \( \ell = 2(Dt)^{1/2} \) and \( t \) can be interpreted as the waiting time for bubble growth as is often done in the literature of nucleate boiling.

Integrating equation (III-37), \( g(m) \) is obtained as

\[
g(m) = 1 - \omega \left[ \text{erf} \frac{m}{\sqrt{tm}} - \frac{1}{\sqrt{tm}} (1 - e^{-m^2}) \right]. \quad (\text{III-60})
\]
Figure 7. Low Supersaturation with an Initially Linear Concentration Field.
Figure 8. Low Supersaturation with an Initially Linear Concentration Field.
Figure 9. Low Supersaturation with an Initially Exponential Concentration Field.
Figure 10. Low Supersaturation with an Initially Exponential Concentration Field.
The bubble history is, therefore,

\[ K^2 = 2J \int_0^\infty m [1 - \omega \text{erf} m - \frac{1}{\sqrt{\pi m}} (1 - e^{-m^2})] \text{erfc} \frac{m}{2r^{1/2}} \, dm . \quad (III-61) \]

A numerical solution is given in Figures 11 and 12.

(4) **Constant Current**

The initial condition is given by equation (III-10):

\[ f(r, \theta) = c_\infty + q \sqrt{\frac{4t}{D}} \text{erf} \frac{r \cos \theta}{2\sqrt{Dt}} , \quad 0 < \theta < \frac{\pi}{2} , \]

\[ = c_\infty + c_q \text{erfc} \frac{r \cos \theta}{l} , \quad (III-62) \]

where \( c_q = q(4t/D)^{1/2} \) and \( l = 2(Dt)^{1/2} \). \( g(m) \) for this case is

\[ g(m) = 1 - \omega \left[ 1 - e^{-m^2} + \frac{\sqrt{\pi}}{2} m \text{erfc} m - \frac{1}{2m} \gamma \left( \frac{3}{2}, m^2 \right) \right] , \quad (III-63) \]

where \( \omega = \frac{c_q}{\sqrt{\pi}} \), and \( \gamma(a,x) \) is the incomplete gamma function

\[ c_\infty + \frac{c_q}{\sqrt{\pi}} - c_s \]

of \( x \); \( \gamma(a,x) = \int_0^x e^{-t} t^{a-1} \, dt \). The bubble history is, therefore

\[ K^2 = 2J \int_0^\infty m [1 - \omega \left[ 1 - e^{-m^2} + \frac{\sqrt{\pi}}{2} m \text{erfc} m - \frac{1}{2m} \gamma \left( \frac{3}{2}, m^2 \right) \right] ] \text{erfc} \frac{m}{2r^{1/2}} \, dm . \quad (III-64) \]

A numerical solution is given in Figures 13 and 14.

(iii) **High Supersaturation**

This is the case where \( \int_0^\infty g(m)e^{-m^2/4\tau} \, dm \) is much larger than \( \int_0^\infty m^2 g(m)e^{-m^2/4\tau} \, dm \). Equation (III-27) thus reduces to

\[ \frac{dK^2}{d\tau} = \frac{J}{2\sqrt{\pi r^3}} \int_0^\infty mg(m)e^{-m^2/4\tau} \, dm , \quad (III-65) \]

which can be integrated to give
Figure 11. Low Supersaturation with Constant Potential.
Figure 12. Low Supersaturation with Constant Potential.
Figure 13. Low Supersaturation with Constant Current.
Figure 14. Low Supersaturation with Constant Current.
\[ \mathcal{L} = J \int_{0}^{\infty} g(m) \text{erfc} \frac{m}{2 \tau^{1/2}} \, dm. \]  

This equation is applied to the same cases treated in Section (ii). We shall merely give the bubbly-history equation whose numerical solutions are presented in Figures 15 to 22.

1. **Linear Concentration Field**

\[ \mathcal{R} = J \left[ \frac{2}{\sqrt{\pi}} \tau^{1/2} - \omega \left( \int_{0}^{1/2} \text{erfc} \frac{m}{2 \tau^{1/2}} \, dm + \int_{1/2}^{\infty} (1 - \frac{1}{2m}) \text{erfc} \frac{m}{2 \tau^{1/2}} \, dm \right) \right]. \]  

2. **Exponential Concentration Field**

\[ \mathcal{R} = J \int_{0}^{\infty} \left[ 1 - \omega (1 - \frac{1}{m} (1 - e^{-m})) \right] \text{erfc} \frac{m}{2 \tau^{1/2}} \, dm. \]  

3. **Constant Potential**

\[ \mathcal{R} = J \int_{0}^{\infty} \left[ 1 - \omega \left( \text{erf} \frac{m}{\sqrt{\pi} m} - \frac{1}{\sqrt{7m}} (1 - e^{-m^2}) \right) \right] \text{erfc} \frac{m}{2 \tau^{1/2}} \, dm. \]  

4. **Constant Current**

\[ \mathcal{R} = J \int_{0}^{\infty} \left[ 1 - \omega \left( 1 - e^{-m^2} + \frac{\sqrt{\pi}}{2} m \text{erfc} \frac{m}{2 \tau^{1/2}} - \frac{3}{2} \frac{\tau^{1/2}}{m} \gamma \left( \frac{3}{2}, \tau^{1/2} \right) \right) \right] \text{erfc} \frac{m}{2 \tau^{1/2}} \, dm. \]  

We have, now, completed our calculation for the bubble dynamics under the condition that the convective transport can be neglected. It is found that for the case of uniform supersaturation, the radius of the bubble is proportional to \((\text{D}t)^{1/2}\) for both the low and the high supersaturation cases. However, the dependence of \(\mathcal{R}\) on the dimensionless driving force, \(J\), is different. It is proportional to \(J^{1/2}\) for the case of low supersaturation but \(J\) for the case of high supersaturation. For
Figure 15. High Supersaturation with an Initially Linear Concentration Field.
Figure 16. High Supersaturation with an Initially Linear Concentration Field.
Figure 17. High Supersaturation with an Initially Exponential Concentration Field.
Figure 18. High Supersaturation with an Initially Exponential Concentration Field.
Figure 19. High Supersaturation with Constant Potential.
Figure 20. High Supersaturation with Constant Potential.
Figure 21. High Supersaturation with Constant Current.
Figure 22. High Supersaturation with Constant Current.
other cases, the dependence on $J$ remains the same as the uniform supersaturation case. However, the radius of the bubble is no longer proportional to $(Dt)^{1/2}$.

Since no generation term is considered in the derivation, the bubble cannot grow indefinitely. For cases where $\omega \leq 1$, the growth will cease after the bubble has completely exhausted the supersaturated concentration in the solution. For cases where $\omega > 1$, a collapse will occur due to the low gas content in the bulk solution.

A comparison of the result with available experimental data will be given later.

d. **Effect of Surface Tension**

If the surface force is important throughout the growth period, a solution to the growth problem becomes very difficult. However, a qualitative discussion will still be useful. The ideal gas law for a gas bubble with an appreciable surface tension can be written as

$$P_v + \frac{2\gamma}{R} = \frac{k}{M} \rho_v T,$$

where $k$ is the universal gas constant. This equation can be rewritten as

$$\rho_v' = \rho_v' + \frac{\xi}{R},$$

where $\rho_v' = \frac{M}{kT_0} P_v$ and $\xi = \frac{2MY}{RT_0} [f(0) - c_s^f] [f(0) - c_s^n]$. The Jakob number for mass transfer is now expressed as

$$J = \frac{\rho_v}{\rho_v' + \frac{\xi}{R}}.$$ 

The growth rate which is often proportional to $J$ is therefore reduced due to the surface force.

**B. Convective Transport Included**

When a bubble is growing at a rapid rate, the transport due to convective diffusion can no longer be neglected. This is often found in the case of nucleate boiling. Under such conditions, it was found by Plesset and Zwick$^{30,31}$ that the thermal diffusion layer is usually small.
in comparison with the bubble radius. An iterative scheme can be developed to solve the bubble dynamics using the assumption of this thin boundary layer.

Skinner and Bankoff\textsuperscript{36} applied Plesset and Zwick’s method to cases of nonuniform initial conditions. Their treatment will be reproduced here briefly so that the similarities to the case where convective transport is neglected can be readily appreciated. The solution has been applied by Skinner and Bankoff to both cases of linear and exponential concentration fields. The numerical solution for the more realistic cases of constant potential and constant current obtained by us will then be given.

a. \textbf{Spherically Symmetric Case}

The convective diffusion equation applied to this case may be written as

\[ \frac{\partial c}{\partial t} + \frac{dR^2}{dr^2} \frac{\partial c}{\partial r} = \frac{D}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right), \]  

(III-73)

with the boundary conditions:

1. at \( t=0, r \geq 0 \), \( c = f(r) \),  
   (III-74)

2. at \( r=R, t > 0 \), \( c = c_s \),  
   (III-75)

3. at \( r=R, t > 0 \), \( D \frac{\partial c}{\partial r} = \rho_v \frac{dR}{dt} \).  
   (III-76)

Equation (III-73) can be simplified greatly by introducing the Lagrangian coordinates \( m(r,t) \) and \( \xi(t) \), where

\[ m(r,t) = \frac{1}{3k^3} (r^3 - R^3(t)) \],  

(III-77)

and

\[ \xi(t) = \frac{D}{k^3} \int_0^t R^h(t) \, dt \].  

(III-78)

and by nondimensionalizing using new variables \( \mathcal{R} \) and \( u(r,t) \) where \( \mathcal{R} = R/k \)

and \( u(m,\xi) = \frac{c(m,\xi) - c_s}{f(0) - c_s} \).  

(III-79)
The result is

$$\frac{\partial}{\partial m} \left[ \left( 1 + \frac{3m}{\mathcal{R}^3} \right)^{4/3} \frac{\partial u}{\partial m} \right] = \frac{\partial u}{\partial \xi},$$

(III-80)

with the boundary conditions:

1. \(u(0, \xi) = 0\),

(III-81)

2. \(u(m, 0) = \frac{f(m) - c}{f(0) - c} = g(m)\),

(III-82)

3. \(\mathcal{R}^3(\xi) = 3J \int_0^\xi \left( \frac{\partial u}{\partial m} (0, \xi) \right) \partial m + \mathcal{R}^3(0)\),

(III-83)

where \(\mathcal{R}(0)\) is the initial radius.

The term \(3m/\mathcal{R}^3\) is a dimensionless distance which is a measure of the distance away from the bubble-solution interface. For a thin boundary layer, equation (III-80) has to be solved only for small values of \(3m/\mathcal{R}^3\). This constitutes a problem of regular perturbation. The zero-order solution can be obtained by neglecting \(3m/\mathcal{R}^3\) as compared to unity in equation (III-80),

$$\frac{\partial^2 u^0}{\partial m^2} = \frac{\partial u^0}{\partial \xi}$$

(III-84)

with the boundary conditions:

1. \(u^0(0, \xi) = 0\),

(III-85)

2. \(u^0(m, 0) = g(m)\),

(III-86)

3. \(\mathcal{R}^3(\xi) = 3J \int_0^\xi \left( \frac{\partial u^0}{\partial m} (0, \xi) \right) \partial \xi'\),

(III-87)

where \(\mathcal{R}(0)\) has been neglected, as justified by Skinner and Bankoff. The solution is once more given in Carslaw and Jaeger,

$$u^0(m, \xi) = \frac{1}{2 \sqrt{\pi} \xi} \int_0^\infty g(m') \left[ \exp \frac{(m'-m)}{-\xi} - \exp \frac{(m'+m)^2}{-\xi} \right] \partial m'. $$

(III-88)
The derivative at \( m=0 \) is thus

\[
\left( \frac{\partial u^0}{\partial m} \right)(0,\bar{\xi}) = \frac{1}{2 \sqrt{\pi} \bar{\xi}^3} \int_{0}^{\infty} g(m)m \exp \left( - \frac{m^2}{4\bar{\xi}^3} \right) dm . \tag{III-89}
\]

The \( \bar{\kappa}-\bar{\xi} \) relationship may now be obtained by integrating equation (III-87):

\[
\bar{\kappa}^{03}(\bar{\xi}) = 3\bar{J} \int_{0}^{\infty} g(m) \text{erfc} \left( \frac{m}{2\bar{\xi}^{1/2}} \right) dm . \tag{III-90}
\]

This result, coupled with the inverse of the transformation of equation (III-78),

\[
\tau(\bar{\xi}) = \frac{\bar{D}_{t}}{\bar{\kappa}} = \int_{0}^{\bar{\xi}} \frac{d\xi'}{\bar{\kappa}^{04}(\xi')} , \tag{III-91}
\]

gives us a parametric representation of the bubble dynamics.

The first-order problem can be formulated by expanding \((1+\frac{3m}{\bar{\kappa}^3})^{4/3}\) in a power series and retaining only terms to first degree in \( m \),

\[
(1+\frac{3m}{\bar{\kappa}^3})^{4/3} = 1 + \frac{4m}{\bar{\kappa}^3} + \frac{2m^2}{\bar{\kappa}^2} - \ldots . \tag{III-92}
\]

The first-order solution must satisfy the following differential equation

\[
\frac{\partial^2 u^1}{\partial m^2} - \frac{\partial u^1}{\partial \bar{\xi}} = \frac{\partial}{\partial m} \left( \frac{4m}{\bar{\kappa}^{03}} \frac{\partial u^0}{\partial m} \right) = - \frac{\partial h(m, \bar{\xi})}{\partial m} , \tag{III-93}
\]

and the boundary conditions:

1. \( u^1(0,\bar{\xi}) = 0 \), \tag{III-94}
2. \( u^1(m,0) = 0 \), \tag{III-95}
3. \( \bar{\kappa}^{13}(\bar{\xi}) = 3\bar{J} \int_{0}^{\bar{\xi}} \left( \frac{\partial u^1}{\partial m} \right)(0,\bar{\xi}) d\xi' \). \tag{III-96}

The solution is

\[
u^1(m,\bar{\xi}) = \int_{0}^{\bar{\xi}} \frac{1}{2\pi(\bar{\xi}-\xi')^{1/2}} \left[ \int_{0}^{\infty} \left[ \exp \frac{(m'-m)^2}{4(\bar{\xi}-\xi')} - \exp \frac{(m'+m)^2}{4(\bar{\xi}-\xi')} \right] d\xi' \right] \frac{\partial h(m',\bar{\xi})}{\partial m} d\xi' . \tag{III-97}
\]
Differentiating $u^1(m,\xi)$ with respect to $m$ and evaluating at $m=0$ yields

$$
\left( \frac{\partial u^1}{\partial m} \right) (0,\xi) = \int_0^\xi \frac{1}{2\pi(\xi-\xi')^{3/2}} \cdot \left[ \int_0^\infty \left( \frac{m^2}{2(\xi-\xi')} - 1 \right) \left( \frac{\partial u^0(m,\xi')}{\partial m} \right) \exp \left[ -\frac{m^2}{4(\xi-\xi')} \right] \, dm \right] \, d\xi',
$$

where $\frac{\partial u^0(m,\xi)}{\partial m}$ may be obtained by differentiating equation (III-88) with respect to $m$,

$$
\frac{\partial u^0(m,\xi)}{\partial m} = \frac{1}{\sqrt{\pi} \xi'} \exp \left( \frac{m^2}{-4\xi'} \right) + \frac{1}{2\sqrt{\pi} \xi'} \int_0^\infty \frac{d\xi(m')}{dm'} \cdot \left[ \exp \left( \frac{(m'-m)^2}{-4\xi'} \right) + \exp \left( \frac{(m'+m)^2}{-4\xi'} \right) \right] \, dm'.
$$

The first-order solution can now be formally obtained by combining equation (III-96) with equations (III-90), (III-98) and (III-99).

It is a formidable task to obtain a numerical evaluation for the first-order solution except for the very simple case of uniform supersaturation. Both the zero- and the first-order solutions for this special case will now be given so that a better understanding of the validity of this perturbation may be achieved.

For uniform supersaturation, $g(m)$ is unity. Equations (III-90) and (III-91) can both be integrated in closed form,

$$
K^0(\xi) = 3J \int_0^\infty \text{erfc} \left( \frac{m}{2\xi^{1/2}} \right) \, dm = \frac{6J}{\sqrt{\pi}} \xi^{1/2},
$$

and

$$
\tau(\xi) = \int_0^\xi K^0(\xi') \, d\xi' = 3 \left( \frac{6J}{\sqrt{\pi}} \right)^{1/3} \xi^{1/3}.
$$
Combining these two equations yields

\[ \mathcal{R}^0 = \sqrt{\frac{12}{\pi}} \, \tau^{1/2}. \]  

(III-102)*

Equation (III-99), for this case, is

\[ \frac{\partial u^0(m, \zeta')}{\partial m} = -\frac{1}{\sqrt{\pi \tau}} \exp \frac{m^2}{4 \tau}. \]  

(III-103)

Equation (III-98) may be integrated after substituting \( \mathcal{R}^0 \) and \( \frac{\partial u^0(m, \zeta')}{\partial m} \) terms from equations (III-100) and (III-103), respectively, to give

\[ \left( \frac{\partial u^1}{\partial m} \right)(0, \zeta) = \frac{4}{9 \sqrt{\pi \tau}} \zeta^{-1/2}. \]  

(III-104)

Finally, the first-order solution can be found by integrating equation (III-96) knowing \( \left( \frac{\partial u^1}{\partial m} \right)(0, \zeta) \),

\[ \mathcal{R}^1(\zeta) = \frac{8}{3\pi^{1/2}} \zeta^{1/2}. \]  

(III-105)

The ratio,

\[ \frac{\mathcal{R}^1}{\mathcal{R}^0} = \frac{h/9}{J}, \]  

(III-106)

shows clearly the diminishing importance of \( \mathcal{R}^1 \) as \( J \) increases. Knowing that we are mainly concerned here with large growth rates where the thin boundary layer approximation is valid, \( \mathcal{R}^1 \) term will be neglected in the following discussions, and the superscript 0 for the zero-order solution will also be dropped. It must be understood that this regular perturbation method is not applicable to bubble collapse because the thickness of the boundary layer increases rather rapidly after the collapse has begun.

b. Axisymmetric Case

The equation of convective diffusion for this case is

* This is the same solution as the one obtained by Plesset and Zwick\(^{31}\) and the exact solution by Scriven\(^{34}\) at high rate of growth.
\[
\frac{\partial c}{\partial t} + \frac{dR^3}{3r^2} \frac{\partial c}{\partial t} \frac{\partial c}{\partial r} = D \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) \right].
\]

(III-107)

with the boundary conditions:

1. at \( r=0, t \geq 0 \), \( c=f(r, \theta) \),

(III-108)

2. at \( r=R, t > 0 \), \( c=c_s \),

(III-109)

3. at \( r=R, t > 0 \), \( \rho \frac{dR}{dt} = \frac{D}{2} \int_0^\pi \left( \frac{\partial c}{\partial r} \right)(R, \theta) \sin \theta \, d\theta \).

(III-110)

This system of equations can be reduced to the spherically symmetric case in a completely analogous manner to the previous case where convective transport is neglected by introducing the transformation:

\[
U(r, t) = \frac{1}{\Delta c} \int_0^\pi \left[ c(r, \theta, t) - c_s \right] \sin \theta \, d\theta,
\]

(III-111)

where

\[
\Delta c = \int_0^\pi \left[ f(0, \theta) - c_s \right] \sin \theta \, d\theta.
\]

(III-112)

The transformed equation is

\[
\frac{\partial U}{\partial t} + \frac{dR^3}{3r^2} \frac{\partial U}{\partial t} = \frac{D}{2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial U}{\partial r} \right),
\]

(III-113)

with the boundary conditions:

1. \( U(r, 0) = \frac{1}{\Delta c} \int_0^\pi \left[ f(r, \theta) - c_s \right] \sin \theta \, d\theta = g(r) \),

(III-114)

2. \( U(R, t) = 0 \),

(III-115)

3. \( \Delta c = 3J \int_0^\infty \left( \frac{\partial U}{\partial r} \right)(R, \theta) \sin \theta \, d\theta \).

(III-116)

The results of these two cases will now be applied to two practical problems.
c. Solutions

(i) Constant Potential

The initial condition is given by equation (III-59),

\[ f(r, \theta) = c_\infty - (c_w - c_\infty) \text{erfc} \frac{r \cos \theta}{\ell} \]  \hspace{1cm} (III-117)

The dimensionless form, \( g(m) \), may now be obtained by substituting equation (III-117) into equation (III-114) using the definition of \( m \) from equation (III-77),

\[ g(m) = 1 - \omega \left[ \text{erf} \left( \frac{3m}{\sqrt{\pi}} \right) - \frac{1}{\sqrt{\pi}} \left( 1 - e^{-\frac{(3m)^2}{3}} \right) \right] \] \hspace{1cm} (III-118)

where \( \omega = \frac{c_w - c_\infty}{c_w - c_b} \). The complete solution can be given formally by

\[ R^3(\xi) = 3 \int \limits_0^\infty \left[ 1 - \omega \left[ \text{erf} \left( \frac{3m}{\sqrt{\pi}} \right) - \frac{1}{\sqrt{\pi}} \left( 1 - e^{-\frac{(3m)^2}{3}} \right) \right] \right] \text{erfc} \frac{m}{2\sqrt{\xi}} \, dm , \] \hspace{1cm} (III-119)

and

\[ \tau(\xi) = \frac{D \xi}{\ell^2} = \int \frac{d\xi'}{K^3(\xi')} . \] \hspace{1cm} (III-120)

A numerical solution is given in Figure 23.

(ii) Constant Current

The initial condition is

\[ f(r, \theta) = c_\infty + c_q \text{erfc} \frac{r \cos \theta}{\ell} \] \hspace{1cm} (III-121)

or, in terms of \( g(m) \),

\[ g(m) = 1 - \omega \left[ 1 - e^{-\frac{(3m)^2}{3}} + \frac{\sqrt{\pi}}{2} \left( \text{erfc} \left( \frac{3m}{\sqrt{\pi}} \right) \right) \right] - \frac{1}{2} \left( \frac{3m}{2} \right)^{1/3} \gamma \left( \frac{3}{2}, \left( \frac{3m}{2} \right)^{2/3} \right) , \] \hspace{1cm} (III-122)

where \( \omega = \frac{-c_q}{\sqrt{\pi}} \). The solution is, therefore,

\[ c_\infty + \frac{c_q}{\sqrt{\pi}} - c_b \]
Figure 23. Constant Potential (thin boundary layer approximation).
\[ R^3(\xi) = 3J \int_0^\infty \left[ 1 - \omega \left( 1 - e^{-\left( \frac{3m}{\Delta} \right)^{2/3}} + \frac{\sqrt{\pi} \left( \frac{3m}{\Delta} \right)^{1/3}}{2} \text{erfc} \left( \frac{3m}{\Delta} \right)^{1/3} \right) \right] \text{erfc} \left( \frac{m}{2\xi^{1/2}} \right) \, dm \]  

and

\[ \tau(\xi) = \frac{D \xi^2}{\Delta^2} = \int_0^\xi \frac{d\xi'}{R^4(\xi')} \]  

A numerical evaluation is given in Figure 24.

In summary, we see that the bubble radius for the uniform supersaturation case is proportional to \((D\xi)^{1/2}\) and also \(\xi\). It should be noted that when \(\omega > 1\), the solution breaks down rapidly after the collapse has begun owing to the failure of the thin boundary layer assumption.

3. Comparison with Available Experimental Data

A. Electrolytic Gas Evolution

Westerheide and Westwater\(^{69}\) and also Glas and Westwater\(^{67}\) measured the growth of various kinds of gas bubbles during electrolysis. For the majority of bubbles they studied, the radius of the bubble was found to be proportional to the square root of time. From the radius-time plot, using Scriven's solution for the asymptotic growth of bubble in a uniformly supersaturated solution, these authors calculated the supersaturation ratio defined as \(c_0/c_s\) for these various types of gas bubbles. Extensive results tabulated in Glas's dissertation\(^{70}\) are summarized in Table 1.

The difference of values of \(c_0/c_s\) between hydrogen and oxygen to chlorine and carbon dioxide can be explained qualitatively by considering the difference in solubilities of hydrogen and oxygen to chlorine and carbon dioxide in electrolytes. Although these supersaturation ratios appear to be quite different from each other, the concentration gradients which are the driving force for mass transport may not be too different.
Figure 24. Constant Current (thin boundary layer approximation).
Table 1.
Various Supersaturation Ratios Reported by Glas."  

<table>
<thead>
<tr>
<th>Gas</th>
<th>$c_{s}^{*}$ in water at 25°C, 1 atm, moles/cc</th>
<th>Average $c_{\infty}/c_{s}$</th>
<th>Number of Bubbles Used in Averaging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$7.13 \times 10^{-7}$</td>
<td>4.65</td>
<td>433</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$11.4 \times 10^{-7}$</td>
<td>5.67</td>
<td>21</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$8.15 \times 10^{-5}$</td>
<td>1.09</td>
<td>86</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>$3.00 \times 10^{-5}$</td>
<td>1.31</td>
<td>112</td>
</tr>
</tbody>
</table>


Glas and Westwater tried to correlate their measured growth coefficient to current density which represents the rate of formation of gas by a so-called "unsteady-state model." The concentration field prior to the formation of the new phase is given by the solution of the diffusion equation (cf. equation (III-10)). The concentration at $x = 10^{-3}$ cm was chosen arbitrarily as the hypothetical uniform supersaturation in Scriven's model to calculate the growth coefficient. The waiting time which was not measured was used as an adjustable parameter to fit the data. Better agreement was obtained for cases of chlorine and oxygen.

Using our model, the Jakob number for the case of constant current can be obtained by combining equation (III-38) and equation (III-62),

\[ J = \frac{1}{\rho_{v}} \int_{0}^{\pi} \left[ f(0, \theta) - c_{s} \right] \sin \theta \, d\theta \]

\[ = \frac{1}{\rho_{v}} \left[ c_{\infty} + \frac{c}{D} \sqrt{\frac{4Dt}{\pi}} - c_{s} \right]. \quad (III-125) \]
Taking the example of hydrogen where \( p_v \) and \( c_s \) are the smallest, using waiting periods ranging from 0.02 to 0.2 sec and a current density of \( 3.95 \times 10^{-2} \text{ amp/cm}^2 \) for the case where the solution is saturated with hydrogen initially, \( J \) varies from 0.095 to 0.30. Therefore, it can be concluded that all the observations made by Westwater and co-workers fall exclusively in our case of low superaturation where the convective transport can be neglected. However, since the actual waiting time has not been measured, a quantitative evaluation using our model was not possible.

B. Nucleate Boiling

To the author's knowledge, no quantitative observations for the bubble growth on boiling surfaces have been made. Dergarabedian measured the growth of bubble in a homogeneous medium. A numerical calculation reveals that the Jakob number for nucleate boiling of water under normal conditions is approximately \( 3.0(T_\infty - T_s) \) where the temperature is expressed in °C. Therefore, for a reasonable degree of superheat, the bubble growth in nucleate boiling will fall in the model of the thin thermal boundary layer where the convective transport is included. Very satisfactory agreement has been obtained using Scriven's model which corresponds to our equation (III-102).

In summary, we have calculated the dynamics of asymptotic bubble growth in an axially symmetric concentration or temperature field. Solutions were presented for the cases of both small and large Jakob numbers which correspond to the cases of electrolytic gas evolution and nucleate boiling, respectively. The results apply to a spherical bubble in a liquid medium of infinite extent or a hemispherical bubble on a surface.

* These are some typical conditions reported in Glas's work.
IV. MASS TRANSFER TO RISING BUBBLES AND DROPS

In the last section, we have treated the dynamics of bubble growth. If a bubble is attached to a horizontal surface facing upward, it cannot grow indefinitely. The buoyancy force will eventually overcome the surface and pressure forces that hold the bubble and separation from the surface will result. A force balance concerning the stability of bubble on surfaces has been established by Kabanov and Frumkin 39. A relationship for maximum bubble size to contact angles and the forces involved was given by Fritz 40 and was verified experimentally in numerous examples of nucleate boiling 41.

After a bubble has left the electrode, additional mass transfer occurs during its rise. As mentioned in Section II, theoretical calculations of mass transfer to rising bubbles have only been carried out either in the Stokes flow regime or in the potential flow regime. In many practical systems, the mass transfer process is performed at moderately high Re. It is also found that analogous procedure of calculation should apply to rising liquid drops as to that of the gas bubbles provided if we take into account the viscosity of the drop and the continuity of the tangential shear stress at the interface. A calculation for the mass transfer to liquid drops would yield useful information in processes such as liquid-liquid extraction.

In this section, the boundary layer approach suggested by Chao 57 and Moore 58 will be used to solve the fluid mechanics for steady flow past a drop or bubble at high Re. The resulting velocity will then be used to solve the convective mass transfer equation. The exact solution thus obtained will be compared with available experimental results.
1. Fluid Mechanics

At high Re, a boundary layer approach was first suggested by Levich. His method was applied by Moore to the case of gas bubbles rising steadily through a liquid. This procedure will be used here for the case of rising liquid drops.

The velocity and pressure are written as perturbations from the potential solution

\[ \bar{v} = \bar{v}^1 + v^1, \quad (IV-1) \]

and

\[ P = \bar{P} + P^1, \quad (IV-2) \]

where \( \bar{v} \) and \( \bar{P} \) are the potential solutions and \( v^1 \) and \( P^1 \) are the perturbed quantities.

The potential solutions given by Hill are

\[ \begin{align*}
\bar{v}_{\theta} &= -\frac{3}{2} v_\infty \left(1 - \frac{2r^2}{R^2}\right) \sin \theta, \\
\bar{v}_r &= \frac{3}{2} v_\infty \left(1 - \frac{2r^2}{R^2}\right) \cos \theta,
\end{align*} \]

for \( r \leq R \), (inside the drop) \( (IV-3) \) and

\[ \begin{align*}
\bar{v}_{\theta} &= v_\infty \left(1 + \frac{r^3}{2r^3}\right) \sin \theta, \\
\bar{v}_r &= -v_\infty \left(1 - \frac{R^3}{r^3}\right) \cos \theta,
\end{align*} \]

for \( r \geq R \), (outside the drop) \( (IV-4) \)

The Navier-Stokes equation of motion and the continuity equation at steady state in spherical coordinates are

\[ \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial r} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta v_r}{r} = -\frac{1}{p r} \frac{\partial P}{\partial \theta} + \sqrt{v^2 v_\theta - \frac{v_\theta}{r^2 \sin^2 \theta} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta}}, \quad (IV-7) \]

\[ \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta^2}{r^2} = -\frac{1}{p r} \frac{\partial P}{\partial r} + \sqrt{v^2 v_r - \frac{2v_r}{r^2} - \frac{2}{r^2} \cot \theta \frac{\partial v_\theta}{\partial \theta}}, \quad (IV-8) \]
and
\[ \frac{\partial v_r}{\partial r} + \frac{2v_r}{r} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (v_\theta \sin \theta) = 0, \quad (IV-9) \]
where
\[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}). \quad (IV-10) \]

The boundary conditions are

1. Far from the interface, the potential solution is valid,
   a. as \( r \to \infty \), \( v_\theta^o = v_\theta^1 = 0 \), \( (IV-11) \)
   b. as \( r \to \infty \), \( v_\theta^i = \frac{1}{r^1} = 0 \). \( (IV-12) \)

2. At the interface, there is no radial velocity and the tangential velocity is continuous,
   a. at \( r=R \), \( \frac{1}{r^o} \frac{\partial v^o_{\theta}}{\partial \theta} = \frac{1}{r^i} \frac{\partial v^i_{\theta}}{\partial \theta} \), \( (IV-13) \)
   b. at \( r=R \), \( \tau^o_{\theta\theta} = \tau^i_{\theta\theta} \). \( (IV-15) \)

At the interface, the tangential shear stress is continuous,
   b. at \( r=R \), \( \tau^o_{\theta\theta} = \tau^i_{\theta\theta} \). \( (IV-15) \)

or, \( \mu_1 \left[ \frac{1}{r^1} \frac{\partial v^1_{\theta}}{\partial \theta} + r \frac{\partial}{\partial r} \left( \frac{v^i_{\theta}}{r^1} \right) \right] = \mu_0 \left[ \frac{1}{r^o} \frac{\partial v^o_{\theta}}{\partial \theta} + r \frac{\partial}{\partial r} \left( \frac{v^o_{\theta}}{r^o} \right) \right]. \) \( (IV-16) \)

This can be simplified by applying equations (IV-1-6) to read:
\[ \mu_0 \frac{\partial v^o_{\theta}}{\partial r} - \mu_1 \frac{\partial v^i_{\theta}}{\partial r} = 3 \frac{v^i_{\theta}}{R} \sin \theta (\mu^o_0 + \frac{3}{2} \mu^i_1). \quad (IV-17) \]

Following Moore's technique \(^{58}\), the magnitudes of each of the terms in equations (IV-7) and (IV-8) are compared. By retaining only terms of order \( \delta \) where \( \delta \) is the thickness of the velocity boundary layer, the following boundary layer equation can be obtained,
Substituting expressions \( \bar{v}_\theta \) and \( \bar{v}_r \) from equations (IV-3) to (IV-6), changing \( r \) to \( y \) where \( y = r - R \) and retaining only terms of order \( y \), equation (IV-18) can be rewritten as

\[
\frac{v_\theta}{r} \frac{\partial v^1_\theta}{\partial \theta} + \frac{v_\theta}{r} \frac{\partial v}{\partial r} + \frac{v_r}{r} \frac{\partial v^1_\theta}{\partial r} = v \frac{\partial^2 v_\theta}{\partial r^2} .
\]  

(IV-18)

This result applies to both inside and outside the drop.

Equation (IV-19) coupled with boundary conditions (equations (IV-11-14) and (IV-17)) can be solved by a suitable transformation into a familiar heat conduction problem whose solution is readily available. First, we let

\[
f^1_{e_0}(\theta, y) = \frac{v^1_\theta}{v_\infty} \sin \theta ,
\]

(IV-20)

and

\[
f^1_{e_1}(\theta, y) = \frac{v^1_\theta}{v_\infty} \sin \theta ,
\]

(IV-21)

and change variable \( \theta, y \) to

\[
\Theta = \frac{1}{3} \left( \frac{2}{3} - \cos \Theta + \frac{1}{3} \cos^3 \Theta \right) ,
\]

(IV-22)

and

\[
Y = \frac{v}{R} \sin^2 \Theta .
\]

(IV-23)

In terms of these new variables, the boundary layer equation and the boundary conditions become

\[
\frac{\partial f^1_{e_0}}{\partial \Theta} = \frac{1}{Re_o} \frac{\partial^2 f^1_{e_0}}{\partial Y^2} , \quad \text{for } Y \geq 0 ,
\]

(IV-24)

and

\[
\frac{\partial f^1_{e_1}}{\partial \Theta} = \frac{1}{Re_i} \frac{\partial^2 f^1_{e_1}}{\partial Y^2} , \quad \text{for } Y \leq 0 ,
\]

(IV-25)
1. at \( Y = \infty \), \( f_0 = 0 \),
   \[ \text{(IV-26)} \]
2. at \( Y = -\infty \), \( f'_1 = 0 \),
   \[ \text{(IV-27)} \]
3. at \( Y = 0 \), \( f_0 = f'_1 \),
   \[ \text{(IV-28)} \]
   \[ \text{at } Y = 0, \quad \mu_0 \left( \frac{\partial f_0}{\partial Y} \right) - \mu_1 \left( \frac{\partial f'_1}{\partial Y} \right) = 3 \left( \mu_0 + \frac{3}{2} \mu_1 \right), \]  
   \[ \text{(IV-29)} \]
4. at \( \theta = 0 \), \( f_0 = f'_1 = 0 \),
   \[ \text{(IV-30)} \]

where the last boundary condition is a direct consequence from the definition of \( f_0 \) and \( f'_1 \), and \( Re_0 = \frac{2\nu_0 R}{v_0} \) and \( Re_1 = \frac{2\nu_0 R}{v_1} \).

The solution of equations (IV-24) and (IV-25) with the boundary conditions, equations (IV-26-30), can readily be found in Carslaw and Jaeger.

\[
\begin{align*}
\Psi_0 &= -6v_\infty \left( \frac{v_0}{Rv_\infty} \right)^{1/2} \sin \theta \left( \frac{1}{2} \phi(\mu, \rho) \right) \text{erfc} \left( \frac{v_0}{2\chi^{1/2}(\theta)} \right), \\
\arching{\Psi}_1 &= -6v_\infty \left( \frac{v_0}{Rv_\infty} \right)^{1/2} \sin \theta \left( \frac{1}{2} \phi(\mu, \rho) \right) \text{erfc} \left( \frac{v_1}{2\chi^{1/2}(\theta)} \right), \\
\end{align*}
\]

where

\[
\begin{align*}
\Psi_0 &= \frac{v_0}{R \left( \frac{v_0}{v_\infty} \right)^{1/2}}, \\
\arching{\Psi}_1 &= \frac{v_1}{R \left( \frac{v_1}{v_\infty} \right)^{1/2}}, \\
\phi(\mu, \rho) &= \left( 1 + \frac{3}{2} \frac{\mu_1}{\mu_0} \right) \left[ 1 + \left( \frac{\rho_1 \mu_1}{\rho_0 \mu_0} \right)^{1/2} \right], \\
\chi(\theta) &= \frac{2}{3} \csc^{4} \theta \left( \frac{2}{3} - \cos \theta + \frac{1}{3} \cos^{3} \theta \right). \\
\end{align*}
\]
This is the tangential component of the velocity. This solution reduces to Moore's gas-liquid case when \( \mu_i \ll \mu_o \) and \( \rho_i \ll \rho_o \).

2. Mass Transfer

For a dilute liquid solution of constant density and diffusivity, the steady convective diffusion equation may be written as

\[
y \cdot \nabla c = D \nabla^2 c.
\]  \hspace{1cm} (IV-38)

The boundary conditions are

1. as \( r \to \infty \), \( c = c_\infty \), \hspace{1cm} (IV-39)
2. at \( r = R \), \( c = c_s \), \hspace{1cm} (IV-40)
3. at \( \theta = 0 \), \( \frac{\partial c}{\partial \theta} = 0 \). \hspace{1cm} (IV-41)

The solution of this problem depends largely on two simplifications. At large Re, for most practical systems, the Pe will even be larger, consequently a thin mass transfer boundary layer results. This leads to two approximations:

1. The first derivatives of concentration can be neglected as compared to the second derivatives,

\[
\frac{2}{r} \frac{\partial c}{\partial r} \ll \frac{\partial^2 c}{\partial r^2}.
\]

2. The stream function which will be defined later can be approximated by the first two terms in an expansion in powers of \( y \).

Equation (IV-38) may now be written in spherical coordinates,

\[
y \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\nu \rho}{r} \frac{\partial c}{\partial \theta} = D \frac{\partial^2 c}{\partial r^2}.
\]  \hspace{1cm} (IV-42)

Here we have omitted from the right side of the equation the angular portion of the Laplacian, \( \frac{1}{r^2 \sin \theta} \left( \sin \theta \frac{\partial c}{\partial \theta} \right) \), since the derivatives along the surface of the sphere are small compared to the derivatives along the radius vector.
The equation of continuity,

$$\frac{1}{r} \frac{\partial}{\partial r} (r^2 v_r) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (v_\theta \sin \theta) = 0, \quad (IV-43)$$

can be replaced by introducing the stream function $\psi$ where

$$v_\theta = -\frac{1}{r \sin \theta} \left( \frac{\partial \psi}{\partial r} \right)_\theta, \quad v_r = \frac{1}{r^2 \sin \theta} \left( \frac{\partial \psi}{\partial \theta} \right)_r \quad (IV-44)$$

Levich showed that equation (IV-42) can be simplified considerably by changing the variable $r$ to $\psi$ and evaluating the equation at $r \approx R$ (or $y \approx 0$). From the chain rule of differential calculus and the definition of the stream function, we have

$$\left( \frac{\partial \psi}{\partial r} \right)_\theta = -r \sin \theta v_\theta \left( \frac{\partial \psi}{\partial \theta} \right)_\theta \quad (IV-45)$$

$$\left( \frac{\partial \psi}{\partial \theta} \right)_r = \left( \frac{\partial \psi}{\partial \theta} \right)_\theta + r^2 \sin \theta v_r \left( \frac{\partial \psi}{\partial \theta} \right)_\theta \quad (IV-46)$$

and

$$\left( \frac{\partial^2 \psi}{\partial r^2} \right)_\theta = \left( \frac{\partial \psi}{\partial \theta} \right)_\theta \left[ -r \sin \theta v_\theta \left( \frac{\partial \psi}{\partial \theta} \right)_\theta \right] = -r \sin \theta v_\theta \left[ \frac{\partial}{\partial \theta} \left( -r \sin \theta v_\theta \left( \frac{\partial \psi}{\partial \theta} \right)_\theta \right) \right] \quad (IV-47)$$

Substituting equations (IV-45-47) into equation (IV-42), replacing $v_\theta$ by $(v_\theta)_{y=0}$ and letting $r=R$, we obtain

$$\frac{\partial \psi}{\partial \theta} = DR^3 (v_\theta)_{y=0} \sin^2 \theta \frac{\partial^2 \psi}{\partial \theta^2}. \quad (IV-48)$$

Using equations (IV-5) and (IV-33) for $v_\theta$ and integrating equation (IV-44) for $\psi$, we obtain

$$(v_\theta)_{y=0} = \frac{3}{2} \nu \omega \sin \theta (1 - \frac{8}{3} \sqrt{\frac{1}{\pi \text{Re}}} \phi(\mu, \rho) \csc^2 \theta (1 - \cos \theta)(2 + \cos \theta)^{1/2}), \quad (IV-49)$$

and

$$(\psi)_{y=0} = \frac{3}{2} \nu \omega R \sin^2 \theta (1 - \frac{8}{3} \sqrt{\frac{1}{\pi \text{Re}}} \phi(\mu, \rho) \csc^2 \theta (1 - \cos \theta)(2 + \cos \theta)^{1/2}). \quad (IV-50)$$
The problem can be simplified further by introducing $t$ where

$$ t = \frac{3}{2} D v_\infty R^3 \int F(\theta) \, d\theta , $$

and

$$ F(\theta) = \sin^3 \theta \left( 1 - \frac{8}{3} \sqrt{\frac{1}{\pi \lambda}} \varphi(\mu, \rho) \csc^2 \theta (1 - \cos \theta)(2 + \cos \theta)^{1/2} \right). $$

Combining equations (IV-49) and (IV-51), equation (IV-48) can be transformed into the one-dimensional heat conduction equation,

$$ \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial y^2} . $$

The boundary conditions (equations (IV-39-41)) can be rewritten in terms of the new variables $t$ and $\psi$,

1. as $\psi = -\infty$, $c_c = \infty$,

2. at $\psi = 0$, $c_c = c_s$,

3. at $t = \frac{3}{2} D v_\infty R^3 \left( \int F(\theta) \, d\theta \right)_{\theta = 0}$, $\frac{\partial c}{\partial t} = 0$.

The solution of equation (IV-53) subjected to the boundary conditions, equations (IV-54-56), can easily be found by the method of similarity transform,

$$ \frac{c - c_s}{c_c - c_s} = \text{erf} \, \eta , $$

where the similarity variable $\eta$ is given by

$$ \eta = \left( \frac{3}{8} \right)^{1/2} \left( \frac{Y_c}{D_R} \right)^{1/2} \frac{\psi}{\sin \theta} \left( \frac{\int F(\theta) \, d\theta - \left( \int F(\theta) \, d\theta \right)_{\theta = 0}}{\left( \int F(\theta) \, d\theta \right)_{\theta = 0}} \right)^{1/2} . $$

The diffusion flux $j$ to the surface is found by differentiating equation (IV-57),

$$ j = D \frac{\partial c}{\partial y} \bigg|_{y = 0} = \left( \frac{3}{2\pi} \right)^{1/2} \left( \frac{D v_\infty}{R} \right)^{1/2} (c_c - c_s) \left( \frac{\int F(\theta) \, d\theta - \left( \int F(\theta) \, d\theta \right)_{\theta = 0}}{\left( \int F(\theta) \, d\theta \right)_{\theta = 0}} \right)^{1/2} . $$
The Nernst diffusion layer thickness \( \delta_N \) defined by

\[
\delta_N = \frac{D(c_\infty - c_s)}{J}
\]

is, therefore, given by

\[
\frac{\delta_N}{R} = 2.05 \left( \frac{\int F(\theta)d\theta - \left( \int F(\theta)d\theta \right)_{\theta=0}}{F(\theta)} \right)^{1/2} \frac{1}{\text{Pe}^{1/2}}.
\]  

(IV-61)

As \( \text{Pe} \to \infty \), \( \delta_N \to 0 \), and as \( \theta \to \pi \), \( \delta_N \to \infty \). The latter contradicts the thin diffusion layer approximation at high Pe. As the rear stagnation point is approached, the magnitude of the tangential and the radial diffusion become equal in importance. The anomaly is caused by neglecting the tangential diffusion term during the derivation of equation (IV-42).

The total mass transfer flux \( F \) to the drop can be found by integrating \( j \) from equation (IV-59) over the total area of the drop,

\[
F = 2\pi R^2 \int_0^\pi j \sin \theta \, d\theta
\]

\[
= \sqrt{6\pi} R^2 \left( \frac{Dv_\infty}{R} \right)^{1/2} (c_\infty - c_s) \int_0^\pi \left( \frac{F(\theta) d\theta}{\int F(\theta)d\theta - \left( \int F(\theta)d\theta \right)_{\theta=0}} \right)^{1/2}.
\]  

(IV-62)

The Nusselt number for mass transfer is, therefore,

\[
\text{Nu} = \frac{2kR}{D} = \frac{2F R}{4\pi R^2 (c_\infty - c_s) D} = \sqrt{\frac{3}{4\pi}} \frac{I(Re, \mu, \rho)}{I(Re, \mu, \rho)} \text{Pe}^{1/2},
\]

(IV-63)

where

\[
I(Re, \mu, \rho) = \int_0^\pi \left( \frac{F(\theta) d\theta}{\int F(\theta)d\theta - \left( \int F(\theta)d\theta \right)_{\theta=0}} \right)^{1/2}.
\]

(IV-64)

As \( Re \to \infty \), this result reduces to the well-known potential solution by Boussinesq,

\[
\text{Nu} = 1.128 \text{Pe}^{1/2}.
\]

(IV-65)
Numerical evaluations for equation (IV-63) are presented in graphical form in Figure 25 to Figure 28. For gas bubbles rising in a liquid, \( \Phi(\mu, \rho) \) is taken as unity due to the small viscosity and density of the gas phase as compared to that of the liquid phase. For liquid drops rising in a liquid medium, the case of \( \mu_1 = \mu_0 \) and \( \rho_1 = \rho_0 \) is used for illustrative purposes. Both cases approach the Boussinesq solution asymptotically as \( Re \to \infty \). At lower \( Re \), the mass transfer is smaller for the liquid-liquid case than for the gas-liquid case due to the slower tangential motion at the liquid-liquid interface. However, the solution does not approach the Stokes solution at low \( Re \) because of the very different approximations used in solving the fluid mechanics for the two cases.

3. Comparison with Available Experimental Data

A. Liquid Drops

Heertjes, Holve and Talsma\textsuperscript{71} reported mass transfer data between isobutanol and water. Their experimental data together with theoretical calculations using our solution, the Stokes flow solution and the Boussinesq potential flow solution are presented in Figures 29 and 30. The present calculation shows a considerable improvement over the calculations based on either the Stokes flow or the potential flow model.

B. Gas Bubbles

Bowman and Johnson\textsuperscript{72} measured the mass transfer to carbon dioxide bubbles in water. Graphical relationship between the relative velocity of rise, the liquid phase mass transfer coefficient and the bubble volume was provided. The bubbles under their experimental conditions are not spherical. An eccentricity factor, not adequately described, was used in their calculation. Fortunately a correlation of such an eccentricity versus the bubble volume was given by Li \textit{et al.}\textsuperscript{73}. Using this information
Figure 25. The Function $\sqrt{\frac{3}{4\pi}} I(Re, \mu, \rho)$ versus $Re$. 
Figure 26. Mass Transfer to Liquid Drops.
Figure 27. Mass Transfer to Gas Bubbles.
Figure 28. Mass Transfer to Drops and Bubbles

Nu versus Re.
Figure 29. Isobutanol Drops in Water.
Figure 30: Water Drops in Isobutanol.
and the diffusivity of \(2.07 \times 10^{-5} \text{ cm}^2/\text{sec}\), we calculated the \(\text{Nu}\) as a function of the \(\text{Re}\) as shown in Figure 31. The potential solution predicts a \(\text{Nu}\) approximately 12% high whereas the present boundary layer approach predicts about 8% high. Levich's solution using Stokes flow is too low. Considering the uncertainties in these measurements, the agreement of the present approach with the data is quite satisfactory.

V. CONCLUSIONS

The principal conclusions of this work can be summarized as follows:

1. An extensive review on the information available in the literature concerning the various steps involved in the formation of a gas phase at a solid-liquid interface and attempts to calculate the mass transfer coefficient for such a process was presented. Special attention was given to the analogies between electrolytic gas evolution and nucleate boiling.

2. Theoretical calculations on the dynamics of bubble growth in a nonuniform concentration or temperature field were performed. For the case of electrolytic gas evolution, the Jakob number for mass transfer was relatively small so that the convective transport can be neglected when compared to the diffusive transport. Solutions were obtained for the linear, the exponential concentration field, the constant potential and the constant current cases at both low and high degrees of supersaturation. For the case of nucleate boiling, the Jakob number for heat transfer was often sufficiently large that the thin thermal boundary layer model became a reasonable one. The parametric solution of Skinner and Bankoff\(^3\) which was obtained by using the technique of regular perturbation was applied to cases of constant potential and constant current. Unfortunately, no experimental data are available to test these theoretical results.
Figure 31. CO$_2$ Bubbles in Water.
3. Mass transfer to drops or bubbles rising steadily through a liquid at high Re and Pe was calculated from a boundary layer solution of the fluid mechanics. Despite the approximations and assumptions used in the derivation, the results compare favorably with experimental observations. The calculation is especially satisfactory at liquid-liquid interfaces where it should yield useful information to many practical processes.

Possible extensions for future investigations are:

1. Measurements of supersaturation at the solid-liquid interface required to initiate the bubble formation at a given current density and electrode surface are desirable. They should reveal the effect of surface imperfections on nucleation.

2. The waiting time for bubble initiation should also be measured at given current densities and electrode surfaces. The author suspects that correlations may exist between the waiting time and the current density and also the electrode surface parameters. It also provides the very essential information for the calculation of the bubble growth using our theoretical results.

3. After the waiting time has been measured, the growth of the bubble should then be followed so that a quantitative test for our theoretical results can be performed.

4. A systematic study on the interfacial phenomena at the gas-electrolyte-electrode interface should yield useful information to the kinetics of adhesion of bubbles and the interactions between bubbles.
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VII. NOMENCLATURE

**English Letters**

- **A**: Interfacial area between two phases.
- **D**: Diffusivity of a species in a homogeneous medium.
- **D**: Hydrodynamic drag force.
- **F**: A function of \( \text{Re} \), \( \mu \), \( \rho \) and \( \theta = \sin^3 \theta \left( 1 - \frac{R}{3} \sqrt{\frac{1}{\text{Re}}} \phi (\mu, \rho) \csc^2 \theta (1 - \cos \theta) \right) \). Total mass transfer to a drop or bubble.
- **I**: A function of \( \text{Re} \), \( \mu \), and \( \rho = \int_0^\pi F(\theta) d\theta \left( \int F(\theta) d\theta - \left( \int F(\theta) d\theta \right)_{\theta=0} \right)^{1/2} \). Rate of nucleation per unit volume.
- **L**: Latent heat of vaporization of a liquid.
- **M**: Molecular weight of a species.
- **N**: Avogadro's number.
- **P**: Pressure in a system.
- **R**: Radius of a bubble, a nucleus or a drop.
- **S**: A similarity variable \( \frac{r_0^\beta}{R} \).
- **S**: Entropy of a system.
- **T**: Temperature of a system.
- **U**: A dimensionless concentration or temperature \( \int_0^\pi \frac{[c(r, \theta, t) - c_s] \sin \theta d\theta}{\int_0^\pi [f(0, \theta) - c_s] \sin \theta d\theta} \).
- **U**: Internal energy of a system.
- **V**: Volume of a system.
- **W**: Work of formation of a nucleus.
- **Y**: A dimensionless distance parameter \( \frac{Y}{R} \sin \theta \).
a: A distance defined in Figure 2.
b: A principal radius of curvature of an interface.
c: Concentration of a species.
d: Diameter of a bubble or a drop.
f: An initial temperature or concentration field for bubble growth.
g: A dimensionless velocity $v_\theta/v_\infty \sin \theta$.
h: A shorthand notation for erf.$c$.
i: Acceleration of gravity.
j: A dimensionless temperature or concentration $\frac{\frac{\pi}{2}}{\int_0^\infty [f(0,\theta)-c_s] \sin \theta \, d\theta}$.
k: A function of angle $6 \sin^2 \theta \chi^2(\theta)$.
l: Local mass transfer flux.
m: Boltzmann's constant.
n: Mass transfer coefficient.
o: A dimensionless Lagrangian coordinate $\frac{r-R}{L}$ or $\frac{1}{3} \frac{r^3-R^3}{L^3}$.
p: Quantity of a species in a system.
q: A constant flux of mass.
r: A variable $\frac{3}{2} D v_\omega R^3 \int F(\theta) \, d\theta$.
s: Time.
t: A dimensionless temperature or concentration $\frac{c(m,\xi)-c_s}{r(0)-c_s}$.
u: Velocity of a fluid.
v: A distance $r-R$.
w: A modified Jakob number $\frac{(J/2\pi)^{\frac{1}{2}}}{L}$.
x: A characteristic length.
y: A dimensionless radius $R/L$.
z: Gas constant.
\gamma: A dimensionless distance $\frac{v}{R} \text{Re}^{\frac{1}{2}}$. 
Greek Letters

\( \Theta \): A function of angle \( \frac{4}{3} (\frac{2}{3} - \cos \theta + \frac{1}{3} \cos^3 \theta) \).

\( \Phi \): A function of \( \mu \) and \( \rho = \left(1 + \frac{3}{2} \frac{\mu_1}{\mu_0}\right) / \left(1 + \left(\frac{\mu_1}{\rho_0 \mu_0}\right)^\frac{1}{2}\right) \).

\( \chi \): A function of angle \( \frac{4}{3} \csc \theta (\frac{2}{3} - \cos \theta + \frac{1}{3} \cos^3 \theta) \).

\( \Omega \): A potential = \( U - TS - \sum_i n_i \mu_i = -PV \).

\( \alpha \): Thermal diffusivity of a fluid.

\( \beta \): Growth coefficient of a bubble.

\( \gamma \): Surface tension of a fluid phase.

\( \delta \): A boundary layer thickness.

\( \varepsilon \): A dimensionless density factor = \( \frac{\rho_f - \rho_v}{\rho_f} \).

\( \xi \): A dimensionless surface parameter = \( \frac{2\mu Y}{\kappa T} \).

\( \zeta \): A dimensionless Lagrangian coordinate = \( \frac{D}{x} \int_0^t R^k(t) \, dt \).

\( \eta \): A similarity variable = \( \left( \frac{3}{8} \right)^\frac{1}{2} \left( \frac{v_0}{DR} \right)^\frac{1}{2} \frac{Y}{\sin \theta} \frac{1}{\sqrt{\frac{\int F(\theta) \, d\theta - \left(\int F(\theta) \, d\theta\right)_{\theta=0}}{\frac{F(\theta)}{\theta}}}} \).

\( \theta \): A contact angle of wetting.

\( \theta \): An angle defined in Figure 2.

\( \kappa \): Thermal conductivity of a fluid.

\( \lambda \): A dimensionless parameter = \( \frac{g b_o^2 (\rho_v - \rho_f)}{\gamma} \).

\( \mu \): Chemical potential of a system.

\( \mu \): Viscosity of a fluid.

\( \nu \): Kinematic viscosity of a fluid.

\( \nu \): Vibrational frequency of a molecule.

\( \xi \): A dimensionless parameter = \( (2\pi)^{\frac{3}{2}} \).

\( \rho \): Density of a fluid.

\( \tau \): A dimensionless time = \( Dt/e^2 \).
\( \tau \): Magnitude of shear stress at fluid-fluid interface.

\( \phi \): An angle defined in Figure 2.

\( \chi \): A function of angle \( \theta = \frac{2}{3} \csc \theta \left( \frac{2}{3} \cos \theta + \frac{1}{3} \cos^3 \theta \right) \).

\( \psi \): Stream function of a fluid in motion.

\( \omega \): A dimensionless temperature or concentration

\[
\omega = \frac{\text{interface concentration} - \text{bulk concentration}}{\text{interface concentration} - \text{saturation concentration}}
\]

**Dimensionless Numbers**

\( J \): Jakob number for heat transfer

\[
J = \frac{k}{\rho c_p \Delta T} \int_0^\pi \left[ f(0, \theta) - c_s \right] \sin \theta \, d\theta.
\]

\( J \): Jakob number for mass transfer

\[
J = \frac{1}{\rho \nu} \int_0^\pi \left[ f(0, \theta) - c_s \right] \sin \theta \, d\theta.
\]

\( \text{Nu} \): Nusselt number for mass transfer

\( \text{Pe} \): Peclet number

\[
\text{Pe} = \text{Re} \times \text{Sc} = v \alpha / D.
\]

\( \text{Re} \): Reynolds number

\[
\text{Re} = \frac{v \alpha}{\nu}.
\]

\( \text{Sc} \): Schmidt number

\[
\text{Sc} = \frac{\nu}{D}.
\]

**Superscripts**

0: Refers to local properties at point 0 in Figure 2.

ad: Refers to properties of an adsorbed molecule.

0: Refers to quantities associated with the zero-order solution.

1: Refers to quantities associated with the first-order solution.

\( \sim \): Refers to the potential solution of ideal fluids.

\( \sim \): Refers to molal quantities.

\( * \): Refers to equilibrium quantities.

**Subscripts**

N: Refers to the Nernst diffusion layer.

g: Refers to values associated with the inert gas phase.

i: Refers to properties inside a drop or bubble.
i: Refers to species i in a system.

ε: Refers to properties in the liquid phase.

max: Refers to quantities at its maximum value.

o: Refers to properties outside a drop or bubble.

q: Refers to the case of constant current.

r: Refers to quantities in the direction of the radial coordinate.

s: Refers to quantities at equilibrium (or saturation).

v: Refers to properties in the vapor phase.

w: Refers to quantities at the solid-liquid interface.

α: Refers to phase α in a system.

β: Refers to phase β in a system.

γ: Refers to phase γ in a system.

θ: Refers to quantities in the angular direction of the polar coordinate.

αβ: Refers to quantities at the interface between phases α and β.

βγ: Refers to quantities at the interface between phases β and γ.

αγ: Refers to quantities at the interface between phases α and γ.

∞: Refers to quantities in the bulk medium.
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