APPLICATION OF POPULATION BALANCE MODELS TO THE STUDY OF NUCLEATION AND GROWTH OF BUBBLES PRODUCED AT GAS EVOLVING ELECTRODES

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University of the Witwatersrand, Johannesburg
for the Degree of Master of Science in Engineering

Johannesburg 1984
DECLARATION

I declare that this dissertation is my own, unaided work, except where specific acknowledgements are made. It is being submitted for the degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

David Lester Hofman

[Signature]

ND day of January, 1984
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Abstract

The rate of mass transfer at gas-evolving electrodes has been shown to be a strong function of the so-called bubble break-off diameter of the gas bubbles leaving the electrode surface. This dissertation shows how the population balance can be applied to the formation of gas bubbles at gas evolving electrodes. This analysis provides a means of predicting the bubble break-off diameter. Experiments were also performed to measure the bubble break-off diameter as well as other parameters, such as the rate of bubble growth, used in the population balance models.

The effect of viscosity, electrolyte flowrate and current on the bubble break-off diameter is also investigated. The flowrate and current have little effect on the bubble break-off diameters, while the break-off diameters show a decrease in size with increasing viscosity. The bubble break-off diameters predicted by the population balance model and those measured were significantly larger than those reported in the literature.
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1. Introduction

The rate at which an electrochemical reaction can occur will depend on the rate at which a reagent can reach the electrode or a product can be removed from it. If the rate at which a species A is brought to the electrode, is limiting, then the rate of production of this species A is given by

\[ R_A = -D_A \frac{dC_A}{dx} \bigg|_{x=0} \]  

(1)

where

- \( R_A \) = rate of production of species A
- \( D_A \) = molecular diffusivity of species A
- \( C_A \) = concentration of species A at position x

By referring to figure 1, equation (1) can be written as

\[ R_A = \frac{D_A}{\delta} (C_{A,s} - C_{A,b}) \]  

(2)

where

- \( C_{A,s} \) = concentration of species A at the electrode surface (x = 0)
- \( C_{A,b} \) = bulk concentration of species A
- \( \delta \) = thickness of the diffusion layer (see figure 1)
Defining the local mass transfer coefficient as

$$k_L \ell = \frac{R_A}{C_{A0} - C_A}$$  \hspace{1cm} (3)

or

$$k_L \ell = \frac{C_A}{A}$$  \hspace{1cm} (4)

The concentration gradient can be normalized by defining

$$C_A^* = \frac{C_A - C_{A0}}{C_{A0} - C_{A\infty}}$$  \hspace{1cm} (5)

and

$$x^* = \frac{x}{h}$$  \hspace{1cm} (6)
The average mass transfer coefficient is thus

\[ \frac{dC_A}{dx} \bigg|_{x^*=0} = \frac{h}{C_{A_0} - C_{A_0}} \frac{dC_A}{dx} \bigg|_{x=0} \]

(by equations (1) and (2))

All from (4)

\[ \frac{dC_A}{dx} \bigg|_{x^*=0} = \left( \frac{k_L}{L} \right) \frac{h}{D_A} \]

(7)

The Sherwood Number is defined as

\[ Sh = \frac{k_L h}{D_A} \]

and substituting for \( k_L \) gives

\[ Sh = \frac{1}{L} \int_0^L \left( \frac{dC_A}{dx} \bigg|_{x^*=0} \right) dz \]

(8)

where \( L \) = length of the electrode in the \( z \) direction

The Sherwood Number is the dimensionless surface concentration gradient over the mass transfer surface.

The rate of mass transfer is clearly affected by the size of \( \delta \). Movement of the electrolyte in the neighbourhood of the electrode can effect the size of \( \delta \). The movement of electrolyte can be brought
about in a number of ways:

(1) Natural convection generated by density variations which may occur due to concentration or temperature changes.

(2) Forced convection caused by pumping, mechanical agitation or air sparging.

(3) Circulation of electrolyte caused by gases generated at the counter electrode.

(4) Agitation of the layer of fluid near the surface of the electrode by the evolution of electrolytically produced gas.

This last means of effecting the mass transfer can considerably enhance the mass transfer because on detachment of the bubble, electrolyte will flow back into the region very rapidly, and in this way is reduced considerably.

In many electrochemical processes the production of gas at an electrode is important. Several examples are the electrolytic manufacture of gases such as chlorine, hydrogen and oxygen; electrowinning, refining and plating of metals which are associated with electrolytic hydrogen production. Vogt (1978) points out that mass transfer at gas evolving electrodes is governed by two phenomena acting simultaneously:

(1) A macroconvective mass transfer caused by the liquid flow parallel to the electrode surface. This influences mass transfer by velocity distributions near the wall. This process is not directly related to the actual gas evolution.

(2) A microconvective mass transfer caused by the liquid in the vicinity of a bubble attached to the electrode being pushed away by the bubble as it grows. This causes a disturbance in the diffusion layer and an increase in the mass transfer rate.
about in a number of ways:

- Natural convection of the electrolyte on the surface of the electrode which may occur due to concentration or temperature changes.
- Forced convection by an external mechanical agitation or sparging.
- Circulation of electrolyte generated by gas evolved at the counter electrode.
- Advective of the liquid near the surface of the electrode by the evolution of electrolytically produced gas.

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2. A microconvective mass transfer caused by the liquid in the vicinity of a bubble attached to the electrode being pushed away by the bubble as it grows. This causes a disturbance in the diffusion layer and an increase in the mass transfer rate.
The macroconvection only has an effect at very low current densities or in turbulent flow conditions. This means that under these conditions the microconvective term is dominant.

1.1 Mass Transfer at Gas Evolving Electrodes

Mass transfer processes at gas evolving electrodes are in many cases analogous to processes in nucleate boiling heat transfer. Bubbles grow from small nucleation sites which are tiny pits in the electrode surface. The gas bubbles increase in size due to mass transfer from the liquid phase either by evaporation (heat transfer) or by desorption of dissolved gas (mass transfer). When the bubbles become large enough for the buoyancy, pressure and inertia forces to overcome the adhesion forces, the bubble leaves the surface. While the bubbles are growing, a convective flow is induced in the surrounding liquid. After the bubble detaches from the surface, liquid flows back to the former bubble centre.

The similarity between the mass and heat transfer processes has led researchers such as Vogt (1970), and Bhattacharya et al. (1977) to develop correlations for mass transfer at gas evolving electrodes based on existing correlations for heat transfer (heat transfer literature). The fact that an electrolyte gas is produced by evolving bubbles has led researchers such as Vogt (1970) and Bhattacharya et al. (1972, 1973) to develop theoretical models for the mass transfer
The macroconvection only has an effect at very low current densities or in turbulent flow conditions. This means that under most operating conditions the microconvective term is dominant.

1.1 Mass Transfer at Gas Evolving Electrodes

Mass transfer processes at gas evolving electrodes are in many respects analogous to processes in nucleate boiling heat transfer. Bubbles grow from small nucleation sites which are tiny pits in the electrode surface. The gas bubbles increase in size due to mass transfer from the liquid phase either by evaporation (heat transfer) or by desorption of dissolved gas (mass transfer). When the bubbles become large enough for the buoyancy, pressure and inertia forces to overcome the adhesion forces, the bubble leaves the surface. While the bubbles are growing a convective flow is induced in the surrounding liquid. After the bubble detaches from the surface, liquid flows back to the former bubble centre.

The similarity between the heat and mass transfer processes has led researchers such as Vogt (1978) and Stephan et al (1979) to develop correlations for mass transfer at gas evolving electrodes based on existing correlations for heat transfer (see section 1.1.1). The fact that an electrolyte flow is induced by ascending bubbles has led researchers such as Janssen et al (1970, 1979) and Fouad et al (1972, 1973) to develop hydrodynamic models based on experimental and
Mass Transfer Correlations of Stephan and Vogt (1979)

Stephan et al (1979) made use of existing heat transfer correlations in order to establish a model for correlating mass transfer at gas evolving electrodes. The assumptions built into the model are:

1. The convection flow induced by the rapidly growing gas bubbles is decisive for mass transfer. The flow in the wake of the detached bubble is unimportant and has negligible effect on the mass transfer.

2. A certain small area may be attributed to each bubble. This microarea is part of the total surface, where a single bubble induces convection flow. The area exists from the time the bubble begins to grow till it detaches from the surface, and is regarded as constant in size. It is not influenced by other bubbles.

3. Due to the small distances and thin boundary layer, the flow along this microarea is assumed laminar.

4. The bubbles are assumed to be spherical or hemispherical.

5. The convection flow near the gas liquid interface is assumed to behave like plug flow, whereas the flow some distance away behaves more like boundary layer flow.

The correlation finally put forward by Stephan et al (1979) is
where $Sh = \frac{0.93 Re^{0.75} Sc^{0.5}}{Gd}$

$Re = \frac{Gdp}{\rho}$

$Sc = \frac{u}{\nu}$

$k_L = mass\ transfer\ coefficient$

$D = molecular\ diffusivity$

$G = volumetric\ flow\ rate\ of\ the\ gas\ per\ unit\ area\ of\ electrode$

$d = bubble\ break\ off\ diameter$

$\rho = liquid\ density$

$u = liquid\ viscosity$

In order to test their correlation, Stephan et al (1979) applied equation (10) to a large volume of data presented in the literature. The errors incurred were fairly large, but no larger than errors incurred in using well established correlations for nucleate boiling which are successfully used in engineering design.

The data used by Stephan et al (1979) was obtained by using electrolytes of similar concentration. The concentrations ranged from 1 mole/l $H_2SO_4$ (with small amounts of salts present) to 4 mole/l $H_3OH$ (with small amounts of salt). Hence the effects of electrolyte density and viscosity (see section 1.4) were not significantly tested.
The evolution of gas bubbles at vertical gas evolving electrodes promotes mass transfer very well. At high rates of gas evolution, the rate of mass transfer is of the same order of magnitude as that obtained by intensive mechanical stirring (Fouad et al, 1972). The reason for this is the rising gas bubbles induce a flow of electrolyte near the electrode surface. This induced flow mixes the liquid in the bulk solution with the liquid in the Nernst diffusion layer, making the diffusion layer thinner. This means that the liquid in contact with the growing bubble has a higher concentration of dissolved gas than previously, and hence the mass transfer rate is higher. Janssen et al (1970) found that the thickness of the Nernst diffusion layer, $\delta$, is dependent on the factors which determine the distance of the ascending bubbles from the surface, the number and size of the bubbles and their size distribution.

Fouad et al (1973) investigated the differences in the mass transfer coefficient obtained on vertical and horizontal electrodes. They observed that horizontal electrodes have higher mass transfer coefficients. This was attributed to the build-up of a hydrodynamic boundary layer and the Nernst diffusion layer whose thickness increases up the vertical electrode's height. This observation would support those of Fouad et al (1972) and Janssen et al (1970).

Janssen and Barendrecht (1979) developed a model for predicting $\delta$. This model is based on the correlation for mass transfer at an electrode:
No = convective Schmidt number = \frac{\nu}{D}

Gr = Grashof number = \rho g \frac{D^3}{\mu} \left( \frac{T_g - T_i}{T_p - T_i} \right)

Sc = Schmidt number = \frac{\nu}{D}

k_L = mass transfer coefficient

D = molecular diffusivity

g = acceleration due to gravity

\rho_L = liquid density

\rho_g = gas density

ν = kinematic viscosity of the liquid = \frac{\nu}{\rho_L}

\nu = dynamic viscosity of the liquid

\ell = characteristic length

Hence \text{No} = \frac{2\ell}{k_L} = \frac{1}{\text{Sc}} \left( \frac{\nu_L + \nu}{\nu L^2 \eta \nu L} \right)^{\frac{1}{2}}

For free convection flow, the曳way force per unit mass of the
bubble resulting from the different densities of the gas and liquid is

\frac{2\ell}{k_L} = \frac{2\ell}{k_L} \left( \frac{\rho_g - \rho_L}{\rho_L} \right)

\text{where} \quad \beta = \text{drag coefficient}

\gamma = volumetric gas fraction of the bubble stream of the
gas evolving electrode.
Also the volumetric flow rate per unit electrode area of electrode $E$ is given by

$$ q = V_e \left( \frac{d}{1 - d} \right) $$

(14)

where $V_e$ = terminal velocity of a single bubble.

and

$$ v_t = \frac{1}{12} \eta d^4 \frac{(P_e - P_g)}{u} $$

(15)

$$ N = \frac{1}{\eta N} \frac{d^4}{HE} $$

(16)

where $d$ = bubble break off diameter (diameter of the rising bubbles),

$N$ = number of active sites per unit surface,

$g$ = frequency of the bubble emission from an active site.

Substituting (13), (14), (15) and (16) into (12) and assuming $e^{-k_0 P}$

Janssen et al. (1979) arrived at the equation

$$ \beta = C \left( \frac{D}{\eta d} \right)^{1/4} $$

(17)

where $C$ = constant evaluated from experiments.

Experiments showed that equation (17) described the mass transfer of gas evolving electrodes very well in lieu of where was no unabsorbed gas present.
Two rate equations for bubble growth are presented below. Both models are theoretically based and have been verified experimentally in the literature.

1.2.1 The rate equation of Scriven (1959)

Scriven (1959) arrived at an expression for the rate of bubble growth by writing a force, mass and energy balance to describe the situation, and then by making a number of simplifying assumptions to make it possible to arrive at a solution. Full details of his derivation are presented in Appendix 1. The solution he arrived at is

\[
r = 28 \sqrt{D t}
\]

where
- \( r \) = radius of the bubble
- \( D \) = mass diffusivity
- \( t \) = time
- \( \varphi \) = dimensionless growth constant

\( \varphi \) is defined by the equation

\[
\frac{\frac{\partial u}{\partial y}}{L_{\text{sat}}} = \frac{1}{2} \exp(\varphi^2 + 2 \varphi) \int_0^\infty x^2 \exp(-x^2 - 2 \varphi x) \, dx
\]

where
- \( \varepsilon = 1 - \frac{p_g}{\rho} \)
- \( \rho_g \) = density of the gas
\[ \rho_L = \text{density of the liquid} \]
\[ \rho_g = \text{bulk concentration of the gas in the liquid} \]
\[ \rho_{sat} = \text{concentration at saturation of the gas in the liquid} \]

where \( x = \frac{\rho_g}{\rho_{sat}} \)

In arriving at this solution, Scribes (1959) has assumed that the process is controlled by the mass transport of dissolved gas from the electrode surface to the bubble surface. In order to simplify his problem, Scribes (1959) made a number of assumptions which are valid for moderate boiling, but whose validity needs to be verified under mass transfer control. An example of such assumptions is the neglecting of viscous, inertia and surface tension terms in the force balance, and the assumption that growing bubbles do not interfere with one another. Full details of these assumptions are discussed in Appendix 1.

Westermayr et al (1961) and Sivas et al (1964) measured bubble growth rates and confirmed the form of equation (19) to be correct. Westermayr et al (1961) did however observe that two bubbles growing close together tended to coalesce for dissolved hydrogen, and hence their growth rates were smaller. Sivas et al (1964) verified the assumption that the surface tension had a negligible effect. They also found that the growth constant, \( K \), was a function of current density, which is not entirely unexpected. They also observed an initial growth period before the bubbles grew according to Scribes's (1959) model. The reason Scribes (1959) does not predict this initial growth period is that one of his initial predictions in his solution was that at time
observed that this initial growth was very rapid (about 2.607 mm), and varied from one electrode surface to another. The reason put forward is that, after polishing, the harder metals (such as nickel) produced smoother surfaces (fewer nucleation sites). This caused a high supersaturation of gas near the electrode, and so once the bubbles started to grow, their growth was rapid until the supersaturation was diminished.

1.2.2 The Rate Equation of Darby and Hague (1973)

Darby et al (1973) tried to elucidate the controlling rate process which limits the maximum rate at which bubbles are evolved at an electrode. They initially expected the rate of bubble growth to be analogous to that observed in nucleate boiling. If this were the case, the bubble radius would grow at a rate proportional to $t^{1/2}$. By observing the phase lag between the electrode current, which is proportional to gas generation, and the bubble growth rate, which corresponds to gas removal, they could deduce whether or not the mass transfer of hydrogen gas to the bubble is limiting (see Appendix 1).

Their experimental results showed

$$r = 0.11 t^{1/2}$$

This result was inconsistent with their initial expectations that the radius would be proportional to $t^{2/3}$. They also observed that
the mass transfer of hydrogen gas to the bubble was not the controlling rate process.

Applying Faraday's Law to the problem:

\[ \text{I}(t) = 2F \frac{\partial \text{N}}{\partial t} \frac{\partial V}{\partial t} \]  \hspace{1cm} (21)

where

- \( V \) = volume of a bubble \( = \frac{4}{3} \pi r^3 \)
- \( t \) = time
- \( \text{N} \) = molar density of the gas
- \( F \) = Faraday's constant
- \( \text{I}(t) \) = instantaneous current which fluctuates with \( V \).

An average instantaneous current, \( \overline{I} \), was used instead of \( \text{I}(t) \) (see Appendix 1), and integrating (21) gives

\[ \overline{I} = \left( \frac{3F}{8 \pi \text{c} \overline{V}} \right) \left( \frac{\partial V}{\partial t} \right) \]

which has the same form as (20). As confirmation to the validity of (21) the coefficients of (20) and (21) were equated, and \( \overline{I} \) was solved for. The value obtained for \( \overline{I} \) agreed with the measured value.

Darcy et al. (1971) then showed that the rate controlling step is a surface reaction, primarily atomic hydrogen combining to form molecular hydrogen on the electrode surface.

The major difference between the two models presented in this section and section 1.2.1 is that the model of Darcy et al. (1971) holds for...
The bubble break off diameter, i.e., the distance at which the bubble leaves the surface, features very prominently in the correlation of Stephan et al. (1979) \[ (10) \]

\[ \sqrt{\frac{\rho g \Delta T}{\mu}} \]

where \( \rho \) is the density, \( g \) is the acceleration due to gravity, \( \Delta T \) is the temperature difference, \( \mu \) is the viscosity, and \( \sigma \) is the surface tension coefficient.

Sides (1981) has shown that the electrical potential on an electrolyte surface varies significantly with position and time.
So when evaluating the mass transfer coefficient, the value of the bubble break off diameter used must either be obtained by experiment, or some average value obtained in the literature. Stephan et al. recommend the values for the break off diameters of bubbles presented in Table 1 to be used in calculations:

Table 1: Bubble Break Off Diameters recommended by Stephan et al. (1979)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Electrolyte</th>
<th>Break off Diameter (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>Alkaline</td>
<td>40</td>
</tr>
<tr>
<td>Oxygen</td>
<td>acidic</td>
<td>40</td>
</tr>
<tr>
<td>Oxygen</td>
<td>alkaline</td>
<td>40</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>acidic</td>
<td>60</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td>40</td>
</tr>
</tbody>
</table>
1.4 The Effect of Viscosity on the Bubble Break Off Diameter

Ault et al (1975) investigated the operation of a zinc electrodeposition process. They found that by increasing the zinc sulphate to acid ratio in the electrolyte, the current efficiency increased until the zinc sulphate to acid ratio reached a certain value, and then the current efficiency decreased. They postulated that the drop in current efficiency was due to nodular growth and attendant short circuiting. The increase in nodular growth (dendritic growth) was believed to be due to the increased viscosity, and hence resistivity, of the electrolyte at a higher zinc sulphate to acid ratio. This postulate would seem to conflict with both equation (10) and equation (11), since both are independent of viscosity. In equation (11), the viscosity effect is cancelled since both the Reynolds and Schmidt numbers are raised to similar powers. The only way this conflict could be resolved is if the bubble break off diameters are affected by viscosity. Earlier work in the Department of Chemical Engineering at the University of the Witwatersrand by Herder et al (1981) has shown that the bubble break off diameter is affected by viscosity.
1.4 The Effect of Viscosity on the Bubble Break-Off Diameter

Ault et al. (1935) investigated the operation of a zinc electrophoresis process. They found that by increasing the zinc sulphate to acid ratio in the electrolyte, the current efficiency increased until the zinc sulphate to acid ratio reached a certain value, and then the current efficiency decreased. They postulated that the drop in current efficiency was due to nodular growth and attendant short circuiting. The increase in nodular growth (dendritic growth) was believed to be due to the increased viscosity, and hence resistivity, of the electrolyte at a higher zinc sulphate to acid ratio. This postulate would seem to conflict with both equation (13) and equation (17), since both are independent of viscosity. In equation (13), the viscosity effect is cancelled since both the Reynolds and Schmidt numbers are raised to similar powers. The only way this conflict could be resolved is if the bubble break-off diameters are affected by viscosity. Earlier work in the Department of Chemical Engineering at the University of the Witwatersrand by Herren et al. (1981) has shown that the bubble break-off diameter is affected by viscosity.
1.6 Scope of this Research

When modelling the production of a particular phase, such as in crystallisation, the growth and nucleation characteristics of a single particle can be incorporated into a population balance to produce an analysis and design procedure for large scale processes. The method of population balances is applied in this work to the electrolytic bubble growth on electrode surfaces and provides a means for predicting growth rates and nucleation rates of bubbles growing on the electrode surface.

To illustrate the above approach to the study of electrolytic gas evolution, the effect of viscosity on bubble break off diameters is investigated. Other parameters such as current density, electrolyte flowrate are also varied and their effect on the process is analysed.
4. Theory

In this section the population balance will be applied to electrolyte bubbles. To begin with, the following symbols must be defined:

\[
\begin{align*}
\phi(l, \delta) &= \text{fraction of bubbles on the surface in the size range } l \text{ to } l + dl \\
\eta(l, \delta) &= \text{fraction of bubbles leaving the surface in the size range } l \text{ to } l + dl \\
\psi(l) &= \text{growth rate of bubble size } l \\
N &= \text{number of nucleation sites per unit area} \\
q &= \text{number of bubbles nucleating per unit area per unit time}
\end{align*}
\]

It should be noted that at steady state the number of bubbles leaving the surface per unit area per unit time is also \( q \). Also,

\[
\int_{-\infty}^{\infty} \phi(l, \delta) \, dl = 1 \quad \text{and} \quad \int_{-\infty}^{\infty} \eta(l, \delta) \, dl = 1
\]

Now the population balance transfer:

| Net rate of bubbles into size | Birth rate in | Death rate to \\
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( l \to l + \delta ) by convection</td>
<td>( \psi(l) ) ( dl )</td>
<td>( \psi(l) ) ( dl )</td>
</tr>
</tbody>
</table>

Expressed this mathematically:

\[
\int_{-\infty}^{\infty} \phi(l, \delta) \, dl - \int_{-\infty}^{\infty} \eta(l, \delta) \, dl = \int_{-\infty}^{\infty} \psi(l) \, dl
\]
\[
\frac{-d}{dt} \left( \frac{\nu(t)}{\ell} \right) + \nu(t) - \ell_0 = \rho g(t) = 0 \quad (1)
\]

where
\[
\int_{\ell_0}^{\ell} \psi(l) \, dl = \begin{cases} 0 & \ell < \ell_0 \\ \psi(\ell_0) & \ell \geq \ell_0
\end{cases}
\]

where \( \ell_0 \) = size of bubbles at nucleation.

There is a hidden assumption in this balance, and it is that the bubbles stop growing after they leave the surface.

Now the boundary condition in (1) is
\[
f(\ell) = 0 \quad \text{when} \quad \ell = \ell_0 \quad (2)
\]

Hence (1) can be integrated from \( \ell = \ell_0 \) to \( \ell = \ell \)

\[
\nu(t) f(\ell) = \rho H(t - \ell_0) - \rho \int_{\ell_0}^{\ell} g(\ell') \, d\ell'
\]

or
\[
f(\ell) = \frac{\rho}{\nu(t)} \left[ H(t - \ell_0) - \frac{\rho}{\nu(t)} \int_{\ell_0}^{\ell} g(\ell') \, d\ell' \right] \quad \text{for} \quad \nu(t) \neq 0
\]

\[
= \frac{\rho}{\nu(t)} \left[ H(t - \ell_0) - \int_{\ell_0}^{\ell} g(\ell') \, d\ell' \right] \quad \text{for} \quad \ell \geq \ell_0
\]

Now
\[
\int_{\ell_0}^{\ell} g(\ell') \, d\ell' = \int_{\ell_0}^{\ell} g(\ell') \, d\ell' - \int_{\ell}^{\infty} g(\ell') \, d\ell'
\]

\[
\sigma_x = \frac{1}{\nu(t)} \int_{\ell}^{\infty} g(\ell') \, d\ell' \quad \ell \geq \ell_0 \quad (4)
\]
It is clear that if all the turtles left the surface at the same time, \( \ell^* \) say, then

\[
g(\ell) = \delta(\ell - \ell^*)
\]

and

\[
f(\ell) = \frac{1}{Nu(\ell)} \left| 1 - H(\ell - \ell^*) \right|
\]

Now let

\[
C(\ell) = \int_{\ell}^{\infty} g(\ell') \, d\ell'
\]

From (1) and (2), integrating by parts gives

\[
\frac{dG(\ell)}{d\ell} = -g(\ell)
\]

The nth moment of \( g(\ell) \), \( \beta_n \), is defined as

\[
\beta_n = \int_{-\infty}^{\infty} \ell^n g(\ell) \, d\ell
\]

From (3),

\[
\beta_n = -n \int_{-\infty}^{\infty} \ell^{n-1} \frac{dG(\ell)}{d\ell} \, d\ell
\]

Integrating by parts gives

\[
\beta_n = \left. \ell^n g(\ell) \right|_{-\infty}^{\infty} - n \int_{-\infty}^{\infty} \ell^{n-1} g(\ell) \, d\ell
\]
Now \( \epsilon^n G(t) = \epsilon^n \int g(t') dt' \) for all \( n \)

So \( \lim_{t \to \infty} G(t) = 0 \) for all \( n \)

\[
\begin{align*}
\lim_{t \to \infty} G(t) &= 0 \\
\lim_{t \to \infty} G(t) &= 1 \\
\lim_{t \to \infty} G(t) &= 0
\end{align*}
\]

But since only \( b_1, b_2, \ldots \) are required,

\[
\int_a^b G(t) dt
\]

Now from (3) \( f(t) = \frac{3}{W(t)} G(t) \)

\[
f(t) = \frac{3}{W(t)} G(t)
\]

Hence substituting \( 3 \) in (10) gives

\[
\frac{3}{W(t)} G(t)
\]

At this point it is necessary to find a model for \( u(t) \), the rate of bubble growth. The two models mentioned in section 1.2 and examined in detail in Appendix 1 will now be rearranged to a form suitable for substitution in equation (9).

Scriven (1959) showed:

\[
u = k \frac{x}{t^2} \quad \text{or} \quad \frac{dx}{dt} = \frac{1}{2} \frac{x}{t} \quad (10)
\]
\[
\frac{dl}{dt} = 2kt^{1/3}
\]

\[
l = 4kt^{1/3} + \text{const} \quad \text{(at } t = t_0)\]

\[
l - l_0 = 4kt^{1/3}
\]

\[
\frac{dl}{dt} = \frac{4k}{l-l_0}
\]

\[
u(t) = \frac{dl}{dt} = \frac{9k^2}{l-l_0}
\]

and \[
\frac{du(t)}{dt} = -\frac{3k^2}{(l-l_0)^{3/2}}
\]

On the other hand Darby et al. (1974) show:

\[
u = k't^{2/3} = \frac{4k}{l-l_0}
\]

\[
\frac{dl}{dt} = 2k't^{1/3}
\]

\[
l = 6k't^{1/3} + \text{const} \quad \text{(at } t = 0) \quad l = l_3
\]

\[
l - l_3 = 6k't^{1/3}
\]

\[
u(t) = \frac{dl}{dt} = 36k^2
\]

\[
(\frac{l}{l-l_3})^{3/2}
\]

\[
u(t) = \frac{dl}{dt} = \frac{72k^3}{(l-l_3)^{3/2}}
\]

\[
\frac{du(t)}{dt} = -\frac{144k^3}{(l-l_3)^{3/2}}
\]

In deriving (9) it was assumed that \( l > l_0 \). It is now assumed that the size of the bubble at nuclear \( t = t_0 \) is negligible, i.e. \( l_0 \rightarrow 0 \).

Hence if (10) is used in (9)
\[ \psi = \frac{k}{q} \left( \frac{1}{q} \right)^{1/2} \int q^{3/2} \, dq \]  

...(1a)

\[ Q = \frac{k}{q} \int q^{1/2} \, dq \quad (1b) \]

In all cases we can assume, the integrals as (1a) and (1b) can be evaluated. This leaves the problem of evaluating the constants in each of these integrals. It can be measured fairly easily, see example 3, and 4, and 5, and 6. And, of course, a problem of applying Faraday's Law to the situation where constants can be introduced.

**Faraday's Law**

\[ \Phi = \frac{\pi}{F} \]

\( \Phi \) - vol. of moles of gas produced in time \( t \)

\( F \) - current flowing for \( t \) s

\( n \) - no. of electrons associated in producing 1 molecule of gas

\( F \) - Faraday constant.

\[ n = \frac{10}{2F} \]

\( n \) - molar density of the gas produced

\( V \) - volume of gas produced in \( t \) s.

\[ V = \frac{MV}{t} \quad (1c) \]

The volume of gas produced per unit area per unit time

\[ V = \int \frac{\partial V}{\partial t} \, dt \]
Hence (12a) and (12b) become

\[
q_{6}^{n} = \frac{1}{\eta(z)\varphi_{o}^{n}} \int_{0}^{\eta(z)\varphi_{o}^{n}} q_{6}^{n} \, \text{d} \xi
\]

\[
q_{8}^{n} = \frac{1}{\eta(z)\varphi_{o}^{n}} \int_{0}^{\eta(z)\varphi_{o}^{n}} q_{8}^{n} \, \text{d} \xi
\]

Now the right-hand sides of (15a) and (15b) are the measured \( q_{6} \) and \( q_{8} \), and can be found, and hence \( \eta(z) \) can be obtained. In evaluating \( \eta(z) \) from a functional or measured \( q_{6} \) and \( q_{8} \) values for \( k \) and \( k' \) can be obtained from (16) and compared with the measured values of \( k \) and \( k' \).
3. **Experimental**

In section 2, it was shown that certain parameters on the steady-state balance needed to be measured. The parameters that were measured were the fraction of bubbles on the surface in the size range \( l \) to \( l + dl \), \( f(l)dl \); the fraction of bubbles leaving the surface in the size range \( l \) to \( l + dl \), \( g(l)dl \); and the number of nucleation sites per unit area, \( N \).

3.1 **Description of the Apparatus**

The bubbles were generated in a perspex cell 900 mm long, 150 mm high and 35 mm wide. The back wall of the cell was a copper plate which served as a cathode on which the bubbles grew. A 20 mm wide lead strip was embedded into the front wall of the cell just to the right of centre to act as the anode. The cathode and anode were connected to a power supply which could produce currents up to 20 A. The electrolyte was circulated through the cell. Flowrates of up to 1 min could be achieved. In order to ensure that the flow across the electrode was laminar, the ends of the cell were packed with marbles and plastic drinking straws. This smoothed out any turbulence that may have arisen at the entrance and exit of the cell. Figure 3.1 is a diagram of the cell.
Figure 3.1    Diagram of the Cell
3.2 Measurement of \( f(l) \, dl \) and \( N \)

Both the parameters \( f(l) \, dl \) and \( N \) could be measured by studying the bubbles on the surface of the cathode. To do this a Wild M7 zoom stereomicroscope was mounted on the anode side of the cell and was focused on the cathode. A camera was attached to the microscope. A Braun P900 high speed flash was used to illuminate the cathode. The high speed flash "froze" any motion which may have caused blurring on the photographs. Photographs were taken of the bubbles on the cathode surface while the current and flowrate were set at some predetermined values. The photographs were developed and printed in the departmental dark room. The bubbles on the surface appeared as well defined spheres, while the bubbles not attached to the surface were cut off focus due to the shallow depth of field caused by the high magnification of the microscope. See figure 3.1 for a typical photograph.

The diameters of the bubbles on the surface were measured with the aid of a video computer and plotter. The photographs were placed on the plotter and with the aid of a digitizing sight, the computer could be told where the edges of each bubble were. A photograph of a ruler (taken under the same conditions as the bubbles) was used as a scale. This technique is fully described in Appendix 1. Having determined the size and number of bubbles on the surface of a known area, \( f(l) \, dl \) and \( N \) could be determined.

\[ N = \text{number of bubbles measured} / \text{area over which measurements were made.} \]

To find \( f(l) \, dl \) the bubbles were sorted into size ranges and a normalized histogram of bubble sizes was drawn.
3.2 Measurement of $f(\xi) d\xi$ and $N$

Both the parameters $f(\xi) d\xi$ and $N$ could be measured by studying the bubbles on the surface of the cathode. To do this a Wild Mf1 zoom stereomicroscope was mounted on the anode side of the cell and was focused on the cathode. A camera was attached to the microscope. A Braun F900 high speed flash was used to illuminate the cathode. The high speed flash "froze" any motion which may have caused blurring on the photographs. Photographs were taken of the bubbles on the cathode surface while the current and flowrate were set at some predetermined values. The photographs were developed and printed in the departmental dark room. The bubbles on the surface appeared as well defined spheres, while the bubbles not attached to the surface were out of focus due to the shallow depth of field caused by the high magnification of the microscope. See figure 3.1 for a typical photograph.

The diameters of the bubbles on the surface were measured with the aid of a micro computer and plotter. The photographs were placed on the plotter and with the aid of a digitizing sight, the computer could be told where the edges of each bubble were. A photograph of a ruler taken under the same conditions as the bubbles was used as a scale. This technique is fully described in Appendix A. Having determined the size and number of bubbles on the surface of a known area, $f(\xi) d\xi$ and $N$ could be determined.

\[
N = \text{number of bubbles measured} / \text{area over which measurements were made.}
\]

To find $f(\xi) d\xi$, the bubbles were sorted into size ranges and a normalised histogram of bubble sizes was drawn.
Figure 4.2: Micrograph of bubbles on the electrode surface
3.3 Measurement of $q(t)dt$

In order to measure $q(t)dt$ it was necessary to measure the size of the bubbles leaving the surface. Clearly the technique outlined in 3.2 would not serve this purpose because even if the depth of field was increased (by lowering the magnification) it would not be possible to differentiate between bubbles on the surface and bubbles off the surface. This problem was overcome by taking a cine of the bubbles on the surface. Because the bubbles grow at a high rate, it was necessary to use high speed photographic techniques. A Fastax 16 mm high speed camera was borrowed from the Mechanical Engineering Department and floodlights for illuminating the cell were borrowed from the Central Graphics Unit. From the cine it was clear which bubbles were attached to the surface and which were not, by virtue of the fact that the attached bubbles were stationary and the other bubbles were moving up. The film was projected onto a screen onto which a grid was drawn to enable the bubble diameters to be measured. The scale was again obtained by filming a ruler. The bubble diameters were sorted into size ranges and a histogram was drawn, which was in fact $q(t)dt$.

3.4 Changing the Viscosity and Electrolyte Composition

The cell could hold three litres of electrolyte solution. In each run 18 ml of sulphuric acid was used in the make up of the electrolyte solution (a concentration of 0.1 mol/l). The rest of the electrolyte consisted of an aqueous solution of either glycerine or magnesium.
sulphate. The amounts of glycerine or magnesium sulphate used were varied so as to obtain the desired viscosity. The actual viscosity was measured using an Ostwald's Viscometer (see Appendix 4).
4. Results

During the experiments the viscosity of the electrolyte was varied using both glycerine and magnesium sulphate. The effect the glycerine and magnesium sulphate had on the results is shown in sections 4.1 and 4.2 below. The effect of current and flowrate on bubbles is shown in section 4.3 while the effect of viscosity is shown in section 4.4. A series of runs was performed using zinc sulphate as an electrolyte, and the effect electroplating had on the bubbles on the electrode surface was observed. These results appear in section 4.5.

Since a distribution of bubble sizes was observed, the average bubble size used to describe a particular run is chosen to be based on a volume distribution rather than on a number distribution. Hence the average bubble size \( \bar{d} \), is defined as

\[
\bar{d} = \frac{\int_{\mathbb{L}} \ell^3 f(\ell) d\ell}{\int_{\mathbb{L}} \ell^2 f(\ell) d\ell}
\]

where \( f(\ell) d\ell \) is the measured number distribution.

So when presenting results, both the number mean bubble diameter and \( \bar{d} \) are tabulated, while only \( \bar{d} \) is used in the graphical presentations.
4.1 Typical Results

In this section samples of typical results obtained during the experiments are presented. The results are for runs using a pure water / sulphuric acid electrolyte (figure 4.1), water / glycerine sulphuric acid electrolyte (figure 4.2) and a water / magnesium sulphate / sulphuric acid electrolyte (figure 4.3). The results show a histogram of the bubble size distribution on the electrode surface and leaving the electrode surface. The size of the bubbles represented in these figures are the measured bubble diameters. Appendix 5 contains a full set of all results gathered over the period of this research.
Figure 4.1  Typical Distribution - Water/H₂SO₄ Electrolyte
Fraction of Bubbles

Hubble Diameter (microns)

Figure 4. Distribution - 350 kg/m MgSO4
4.2 The Effect of using Glycerine or Magnesium Sulphate to Increase the Viscosity of the Electrolyte

In this section the effect of using either glycerine or magnesium sulphate to alter the viscosity is shown. The results are given for the current fixed at 1 A and the flowrate set at 1.6 l/min. Table A.1 shows the effect of glycerine concentration on the bubbles measured attached to and leaving the surface. The same effect is shown in table 4.2 for various magnesium sulphate concentrations. Figure 4.4 graphically illustrates these effects.

Clearly the mean bubble diameters, both on and leaving the surface, drop with increasing viscosity. The bubbles leaving the surface are larger than the bubbles on the surface, (as was evident from figures 4.1, 4.2 and 4.3). It is interesting to note that although the bubbles on the surface for the magnesium sulphate case are smaller than the bubbles on the surface for glycerine, the bubbles leaving the surface in the magnesium sulphate case are larger.
### Table 4.1 Effect of Changing the Glycerine Concentration

<table>
<thead>
<tr>
<th>Concentration of Glycerine (kg/m²)</th>
<th>Viscosity (cP)</th>
<th>Mean bubble diameter on the surface (mm)</th>
<th>Standard deviation of bubble diameters on the surface (mm)</th>
<th>Mean bubble diameter leaving the surface (mm)</th>
<th>Standard deviation of bubble diameters leaving the surface (mm)</th>
<th>Mean bubble diameter leaving the surface (mm)</th>
<th>Standard deviation of bubble diameters leaving the surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.32</td>
<td>99</td>
<td>15</td>
<td>103</td>
<td>127</td>
<td>145</td>
<td>155</td>
</tr>
<tr>
<td>16.7</td>
<td>1.2</td>
<td>89</td>
<td>18</td>
<td>95</td>
<td>102</td>
<td>100</td>
<td>147</td>
</tr>
<tr>
<td>12.2</td>
<td>1.2</td>
<td>89</td>
<td>15</td>
<td>95</td>
<td>95</td>
<td>70</td>
<td>135</td>
</tr>
<tr>
<td>12.2</td>
<td>1.2</td>
<td>77</td>
<td>13</td>
<td>80</td>
<td>90</td>
<td>90</td>
<td>113</td>
</tr>
<tr>
<td>11.2</td>
<td>1.2</td>
<td>71</td>
<td>13</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>118</td>
</tr>
<tr>
<td>7.0</td>
<td>0.32</td>
<td>99</td>
<td>22</td>
<td>103</td>
<td>127</td>
<td>145</td>
<td>155</td>
</tr>
<tr>
<td>15.0</td>
<td>1.02</td>
<td>80</td>
<td>16</td>
<td>92</td>
<td>114</td>
<td>45</td>
<td>149</td>
</tr>
<tr>
<td>11.0</td>
<td>1.02</td>
<td>80</td>
<td>14</td>
<td>103</td>
<td>103</td>
<td>41</td>
<td>149</td>
</tr>
<tr>
<td>7.0</td>
<td>0.32</td>
<td>99</td>
<td>11</td>
<td>73</td>
<td>99</td>
<td>31</td>
<td>123</td>
</tr>
<tr>
<td>2.17</td>
<td>67</td>
<td>19</td>
<td>71</td>
<td>71</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
</tbody>
</table>

### Table 4.2 Effect of Changing the 3,5-DCMU Concentration

<table>
<thead>
<tr>
<th>Concentration of 3,5-DCMU (kg/m²)</th>
<th>Viscosity (cP)</th>
<th>Mean bubble diameter on the surface (mm)</th>
<th>Standard deviation of bubble diameters on the surface (mm)</th>
<th>Mean bubble diameter leaving the surface (mm)</th>
<th>Standard deviation of bubble diameters leaving the surface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.92</td>
<td>99</td>
<td>22</td>
<td>103</td>
<td>127</td>
</tr>
<tr>
<td>15.0</td>
<td>1.02</td>
<td>80</td>
<td>16</td>
<td>92</td>
<td>114</td>
</tr>
<tr>
<td>15.0</td>
<td>1.02</td>
<td>80</td>
<td>14</td>
<td>103</td>
<td>103</td>
</tr>
<tr>
<td>7.0</td>
<td>0.92</td>
<td>99</td>
<td>14</td>
<td>73</td>
<td>99</td>
</tr>
<tr>
<td>2.17</td>
<td>67</td>
<td>19</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>0.0</td>
<td>0.92</td>
<td>99</td>
<td>22</td>
<td>103</td>
<td>127</td>
</tr>
<tr>
<td>15.0</td>
<td>1.02</td>
<td>80</td>
<td>16</td>
<td>92</td>
<td>114</td>
</tr>
<tr>
<td>15.0</td>
<td>1.02</td>
<td>80</td>
<td>14</td>
<td>103</td>
<td>103</td>
</tr>
<tr>
<td>7.0</td>
<td>0.92</td>
<td>99</td>
<td>14</td>
<td>73</td>
<td>99</td>
</tr>
<tr>
<td>2.17</td>
<td>67</td>
<td>19</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
</tbody>
</table>

The tables above provide data on the effect of changing the glycerine concentration and the 3,5-DCMU concentration on the mean bubble diameters and their standard deviations on the surface and leaving the surface.
Figure 4.4 Effect of using Glycerine or MgSO₄ to alter the Viscosity
4.3 Effect of Flowrate and Current

Runs were performed to observe the effect the current and flowrate had on the bubble sizes at two different viscosities. The first was performed at the lowest viscosity (0.92 cP) where the electrolyte was a water / sulphuric acid solution. The second was performed at a high viscosity (5.8 cP) where the viscosity was raised by adding glycerine to the electrolyte. The results from these two runs are tabulated in tables 4.3 and 4.4 below.

### Table 4.3 Effect of Current and Flowrate (Viscosity = 0.9 cP)

<table>
<thead>
<tr>
<th>Flowrate (l/min)</th>
<th>(d) on the surface ((\mu\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current (A)</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>2.00</td>
<td>103</td>
</tr>
<tr>
<td>3.75</td>
<td>97</td>
</tr>
<tr>
<td>4.60</td>
<td>104</td>
</tr>
</tbody>
</table>

### Table 4.4 Effect of Current and Flowrate (Viscosity = 5.8 cP)

<table>
<thead>
<tr>
<th>Flowrate (l/min)</th>
<th>(d) on the surface ((\mu\text{m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current (A)</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>1.18</td>
<td>83</td>
</tr>
<tr>
<td>2.00</td>
<td>87</td>
</tr>
<tr>
<td>2.90</td>
<td>85</td>
</tr>
</tbody>
</table>
From these results it is clear that the current had negligible effect on the bubble sizes on the surface, and did not effect the size distribution significantly (see Appendix 5 for size distribution results). At the low viscosity, the flowrate seemed to have a small effect on the bubble sizes on the surface. As the flowrate increases, the bubble size decreases.

Since the effect of flowrate and current was small on the size of the bubbles on the surface, it was assumed that this would be the case with the bubbles leaving the surface, and hence the bulk of the experiments were performed at a fixed current and flowrate - 1.0 A and 1.5 l/min.
4.4 The Effect of Electroplating

A series of runs were performed in which the viscosity of the electrolyte was varied using zinc sulphate rather than magnesium sulphate or glycerine. In these runs the zinc plated out on the cathode. The average bubble diameters observed on the electrode surface are tabulated below in table 4.5, and shown graphically in figure 4.3.

Table 4.5 Effect of Electroplating

<table>
<thead>
<tr>
<th>Concentration of ZnSO₄·7H₂O (kg/m³)</th>
<th>Viscosity 'cP</th>
<th>Mean bubble diameter on the surface (number distribution) (µm)</th>
<th>Standard deviation of bubble diameters on the surface (number distribution) (µm)</th>
<th>d on the surface (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.92</td>
<td>99</td>
<td>22</td>
<td>103</td>
</tr>
<tr>
<td>4.0</td>
<td>0.95</td>
<td>84</td>
<td>19</td>
<td>96</td>
</tr>
<tr>
<td>84.0</td>
<td>1.06</td>
<td>75</td>
<td>14</td>
<td>82</td>
</tr>
<tr>
<td>184.0</td>
<td>1.41</td>
<td>72</td>
<td>13</td>
<td>78</td>
</tr>
<tr>
<td>386.0</td>
<td>2.20</td>
<td>74</td>
<td>16</td>
<td>83</td>
</tr>
<tr>
<td>507.0</td>
<td>2.50</td>
<td>73</td>
<td>15</td>
<td>81</td>
</tr>
<tr>
<td>863.0</td>
<td>5.00</td>
<td>67</td>
<td>6</td>
<td>69</td>
</tr>
</tbody>
</table>

At the low viscosities (low zinc sulphate concentrations) the area of the cathode which was being plated could not be seen through the microscope. As the viscosity (zinc sulphate concentration) increased, the area being plated grew and could be observed. In the experiments, the runs performed at viscosities below 1.41 cP no coating was observed in the field of
measurement, while at the viscosities above 2.2 cP plating was observed. In both cases the bubble diameters decrease with viscosity. The overall trend seems to be much the same as for the cases where magnesium sulphate or glycerine were used.
Figure 4.5  The effect of electroplating
4.5 The number of Nucleation Sites per Unit Area

From the photographs of the bubbles on the surface, the number of nucleation sites per unit area of electrode surface, N, can be measured. This is done by simply counting the number of bubbles on a known area of the electrode. Since more than one photograph was taken during a run, an average was taken over each run. The values of N tabulated in table 4.6 are for runs at flowrates of 2.00 l/min and currents of 1.5 A. Figure 4.6 is a graphical representation of this.

Table 4.6 The number of Nucleation Sites per Unit Area

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Viscosity (cP)</th>
<th>N (m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/H₂SO₄</td>
<td>0.92</td>
<td>8.966 x 10⁶</td>
</tr>
<tr>
<td>Glycerine/H₂SO₄</td>
<td>1.00</td>
<td>8.998 x 10⁶</td>
</tr>
<tr>
<td>Glycerine/H₂SO₄</td>
<td>1.62</td>
<td>8.120 x 10⁶</td>
</tr>
<tr>
<td>Glycerine/H₂SO₄</td>
<td>1.40</td>
<td>7.480 x 10⁶</td>
</tr>
<tr>
<td>Glycerine/H₂SO₄</td>
<td>1.37</td>
<td>7.114 x 10⁶</td>
</tr>
<tr>
<td>MgSO₄/H₂O/H₂SO₄</td>
<td>1.02</td>
<td>8.845 x 10⁶</td>
</tr>
<tr>
<td>MgSO₄/H₂O/H₂SO₄</td>
<td>2.07</td>
<td>7.697 x 10⁶</td>
</tr>
<tr>
<td>MgSO₄/H₂O/H₂SO₄</td>
<td>2.54</td>
<td>7.374 x 10⁶</td>
</tr>
</tbody>
</table>

From the results it is clear that the effect of using either glycerine or magnesium sulphate in the electrolyte has a negligible effect on N.
Figure 4.6 The effect of Viscosity on $N$


$f(t)dt$ was measured (see section 3) and so the integral on the right side of equations (1a) and (1b) could be numerically evaluated. The current density was measured (see Appendix 6) and $\dot{I}$ could be evaluated. The measured size distribution on the surface of the electrode, in a way, the right hand sides of equations (1a) and (1b) could be evaluated.

From the distributions measured leaving the surface, $g_n$ could be evaluated. To do this a functional form was given to $g(l)dl$, the fraction of bubbling leaving the surface in the size range $l$ to $l + dl$. It was found that either a normal or a gamma density function fitted $g(l)dl$ quite well, the difference in using either one or the other was small. Hence $\delta_n$ was evaluated, $q$ could be evaluated by dividing the right hand side of the equation

An average value for $q$ is taken over the first two moments. $q$ is also evaluated from the expression

$$q = \frac{6l}{z_0 m F^{3/2}}$$

which was derived in section 2. In section 2 it was also shown that

$$Nk^{1/2} = \frac{l}{72 \pi z_0 F}$$

or

$$Nk^{1/3} = \frac{l}{4 \pi z_0 F}$$

Since $N$ was measured (see sections 3 and 4) the values of $k$ or $k'$ (depending on which rate equation was used) could be evaluated.

A computer program was written to perform these calculations. This program is presented in Appendix 7 together with a description as to the integrals in (1a) and (1b) were performed, and how $\delta_n$ was evaluated.
The results obtained from this program are summarised in tables 5.1 and 5.2 below. The values of $q$ calculated by equations (1a) and (1b) which are reported, are the mean values of $q$ calculated over the first two moments.

Table 5.1 Calculated values for $k$ and $k'$

<table>
<thead>
<tr>
<th>Concentration of glycerine or MgSO₄</th>
<th>Viscosity (cP)</th>
<th>$N$ (m⁻²)</th>
<th>$k$ (ms⁻¹)</th>
<th>$k'$ (ms⁻¹/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 kg/m³ glycerine</td>
<td>0.92</td>
<td>8.966x10⁶</td>
<td>3.20x10⁻⁵</td>
<td>4.49x10⁻⁵</td>
</tr>
<tr>
<td>36.7 kg/m³ glycerine</td>
<td>1.00</td>
<td>8.898x10⁵</td>
<td>3.29x10⁻⁵</td>
<td>4.50x10⁻⁵</td>
</tr>
<tr>
<td>198.8 kg/m³ glycerine</td>
<td>1.62</td>
<td>8.120x10⁶</td>
<td>3.61x10⁻⁵</td>
<td>4.64x10⁻⁵</td>
</tr>
<tr>
<td>332.0 kg/m³ glycerine</td>
<td>2.40</td>
<td>7.480x10⁶</td>
<td>3.85x10⁻⁵</td>
<td>4.73x10⁻⁵</td>
</tr>
<tr>
<td>366.0 kg/m³ glycerine</td>
<td>2.97</td>
<td>7.114x10⁶</td>
<td>3.96x10⁻⁵</td>
<td>4.85x10⁻⁵</td>
</tr>
<tr>
<td>10.0 kg/m³ MgSO₄ · 7H₂O</td>
<td>1.02</td>
<td>8.845x10⁶</td>
<td>3.56x10⁻⁵</td>
<td>4.51x10⁻⁵</td>
</tr>
<tr>
<td>280.0 kg/m³ MgSO₄ · 7H₂O</td>
<td>2.07</td>
<td>7.697x10⁶</td>
<td>3.84x10⁻⁵</td>
<td>4.73x10⁻⁵</td>
</tr>
<tr>
<td>350.0 kg/m³ MgSO₄ · 7H₂O</td>
<td>2.54</td>
<td>7.374x10⁶</td>
<td>4.03x10⁻⁵</td>
<td>4.73x10⁻⁵</td>
</tr>
</tbody>
</table>
Table 5.2  Calculated Values for $q$

<table>
<thead>
<tr>
<th>Concentration of glycerine or $\text{MgSO}_4$</th>
<th>Viscosity (cP)</th>
<th>Distribution assumed for $q(t)dt$</th>
<th>$q$ from equation (3) ($\text{m}^{-3}\text{s}^{-1}$)</th>
<th>$q$ from equation (1a) ($\text{m}^{-3}\text{s}^{-1}$)</th>
<th>$q$ from equation (1b) ($\text{m}^{-3}\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0$</td>
<td>0.92</td>
<td>Normal</td>
<td>3.874x10$^6$</td>
<td>3.999x10$^6$</td>
<td>4.353x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>1.796x10$^6$</td>
<td>3.979x10$^6$</td>
<td>4.332x10$^6$</td>
</tr>
<tr>
<td>$36.7 \text{ kg/m}^3$ glycerine</td>
<td>1.00</td>
<td>Normal</td>
<td>5.144x10$^6$</td>
<td>3.477x10$^6$</td>
<td>3.657x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>4.961x10$^6$</td>
<td>3.457x10$^6$</td>
<td>3.636x10$^6$</td>
</tr>
<tr>
<td>$198.8 \text{ kg/m}^3$ glycerine</td>
<td>1.62</td>
<td>Normal</td>
<td>7.535x10$^6$</td>
<td>4.778x10$^6$</td>
<td>5.096x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>7.107x10$^6$</td>
<td>4.746x10$^6$</td>
<td>5.063x10$^6$</td>
</tr>
<tr>
<td>$332.0 \text{ kg/m}^3$ glycerine</td>
<td>2.40</td>
<td>Normal</td>
<td>9.691x10$^6$</td>
<td>5.000x10$^6$</td>
<td>5.10x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>9.328x10$^6$</td>
<td>4.861x10$^6$</td>
<td>5.07x10$^6$</td>
</tr>
<tr>
<td>$386.0 \text{ kg/m}^3$ glycerine</td>
<td>2.97</td>
<td>Normal</td>
<td>1.008x10$^7$</td>
<td>5.02x10$^6$</td>
<td>5.30x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>9.682x10$^6$</td>
<td>4.999x10$^6$</td>
<td>5.26x10$^6$</td>
</tr>
<tr>
<td>$10.0 \text{ kg/m}^3$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$</td>
<td>1.02</td>
<td>Normal</td>
<td>4.916x10$^6$</td>
<td>3.776x10$^6$</td>
<td>4.062x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>4.729x10$^6$</td>
<td>3.750x10$^6$</td>
<td>4.034x10$^6$</td>
</tr>
<tr>
<td>$280.0 \text{ kg/m}^3$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$</td>
<td>2.07</td>
<td>Normal</td>
<td>5.809x10$^6$</td>
<td>4.730x10$^6$</td>
<td>4.978x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>5.543x10$^6$</td>
<td>4.695x10$^6$</td>
<td>4.942x10$^6$</td>
</tr>
<tr>
<td>$350.0 \text{ kg/m}^3$ $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$</td>
<td>2.54</td>
<td>Normal</td>
<td>7.916x10$^6$</td>
<td>4.503x10$^6$</td>
<td>4.713x10$^6$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gamma</td>
<td>7.479x10$^6$</td>
<td>4.474x10$^6$</td>
<td>4.682x10$^6$</td>
</tr>
</tbody>
</table>
In Appendix 1 it is seen that $k'$ must take on a value of $2.22 \times 10^{-1} \text{s}^{-1/2}$. Since the current used in all the runs tabulated in table 5.1 was 1 A, $k'$ must equal $2.22 \times 10^{-1} \text{s}^{-1/2}$ if the rate of bubble growth is described by equation (2b). Clearly the value of $k'$ calculated is significantly smaller than this, and hence it is concluded that the bubbles do not grow according to equation (2b). Also in Appendix 1 a table of values for $k$ obtained from the literature is presented. These values correspond to the measured values of $k$ presented in table 5.1. This suggests that the bubbles are in fact growing according to equation (2a).

In figure 5.1, $k$ is plotted against the viscosity of the two electrolytes used. Over the range of viscosity used, $k$ does not change all that much -- $k$ increases by 24 per cent when glycerine is used in the electrolyte and increases by 26 per cent when magnesium sulphate is used in the electrolyte.

The values of $q$, the rate of bubble nucleation per unit area, calculated from equation (1b) (ie assuming a rate of bubble growth given by equation (2b)) can now be rejected since it has been established that the rate of bubble growth is well represented by equation (2a). It is clear from table 5.2 that the assumption of a normal or gamma distribution for the bubbles leaving the electrode surface has almost no effect on $q$. The values of $q$ evaluated using equation (3) show more of an effect of viscosity than do the ones evaluated from equation (1a). This effect is shown in figure 5.2 where the values of $q$ are calculated using the normal distribution assumption for $g(\ell)$.
Figure 5.1  The effect of Viscosity on k

- Glycerine used
- MgSO₄ used

Viscosity (cP)

5.00  4.00  3.00

-1.0 × 10⁻⁵  1/2  8 9
Figure 5.2  The effect of Viscosity on $z$
The values of \( q \) obtained from equation (3) depend on the third moment of \( g(l) \), i.e. \( \delta_3 \). Since \( \delta_3 \) is very much smaller than \( \delta_1 \) and \( \delta_2 \), numerical errors are expected to creep into this value of \( q \). The values of \( q \) obtained from equation (1a) vary by about 0.5 per cent over the viscosity range used, and the use of glycerine or magnesium sulphate in the electrolyte has negligible effect.

To use the population balance as a means of predicting bubble break off diameters, \( k \) can be obtained from Glas et al (1964) for the current used. An experiment as described in section 3.2 needs to be done to establish \( N \) for the electrode and electrolyte used. As a result of this experiment the bubble size distribution on the electrode surface can also be obtained. This leaves three parameters to be solved for using the population balance: \( N \); the mean bubble diameter leaving the electrode surface, \( \eta \); and the standard deviation of the bubble sizes leaving the surface, \( \sigma \).

Using equation (1a) the first three moments of the distribution of bubble sizes can be found:

\[
\delta_1 = \frac{\delta_1}{\tau \sigma_0} \int q \frac{g(l)}{l} dl \tag{5}
\]

\[
\delta_2 = \frac{\delta_2}{\tau \sigma_0} \int q \left( \frac{g(l)}{l} \right)^2 dl \tag{6}
\]

\[
\delta_3 = \frac{\delta_3}{\tau \sigma_0} \int q \left( \frac{g(l)}{l} \right)^3 dl \tag{7}
\]

Now in Appendix 2 it is shown that

\[
\delta_1 = \eta \tag{8}
\]

\[
\delta_2 = \eta^2 + \sigma \tag{9}
\]

\[
\delta_3 = \eta^3 + 3\eta \sigma \tag{10}
\]
Substituting (8), (9) and (10) into (5), (6) and (7) gives three equations in the unknowns $q$, $n$ and $c$.

Having solved these three equations (which will require some sort of iterative numerical technique), the bubble break off diameter, $d$, can be calculated as:

$$ d = \frac{\frac{\partial \psi}{\partial y}}{\frac{n^2 + 6n^2q^2 + 3c^2}{n^2 + 3n^2}} $$
Substituting (8), (9) and (10) into (5), (6) and (7) gives three equations in the unknowns \( q, \eta \) and \( \alpha \).

Having solved these three equations (which will require some sort of iterative numerical technique), the bubble break off diameter, \( d \), can be calculated as

\[
d = \frac{\bar{a}}{\bar{c}_1} = \frac{n^2 + 6\eta^2 \frac{a_1}{a} + 3a^2}{\eta^2 + 3\eta a^2}
\]
6. Discussion and Conclusion

In situations where the production of a new phase results in the formation of particles such as gas bubbles, liquid droplets or solid crystals, the size of these particles is of considerable importance to the optimum performance of the process. At gas-evolving electrodes the rate of mass transfer has been shown to be a strong function of the bubble break off diameter. For this reason a method of modelling the process would be useful. Population balance models, which incorporate growth and nucleation characteristics have been successfully applied to the analysis of crystallisation processes. In section 5 the population balance is applied to the production of bubbles at gas-evolving electrodes. The population balance enables one to predict the bubble break off diameter after having determined three parameters. These parameters are the number of nucleation sites per unit area, the rate of nucleation per unit area and a rate constant associated with a model for the rate of bubble growth on the electrode surface.

In Appendix 1, two models for the rate of bubble growth on an electrode surface appearing in the literature have been reviewed. In section it was found that the model of Scriven (1959) fitted the experimental data very well. The rate constant calculated from the experimental data compared favourably with that reported in the literature (see section 5). This rate constant showed negligible variation with electrolyte viscosity.
The number of nucleation sites per unit electrode area, \( N \), is a function of the electrode type used. It was also found to be a function of the electrolyte viscosity. With increasing viscosity, \( N \) showed a drop of about 20 per cent over the viscosity range used. The increase in viscosity seemed to cause previously active sites to become inactive. A possible reason is that mass transfer of dissolved gas was reduced by the increased viscosity, and hence only certain sites near high local gas concentrations were able to receive gas for the bubbles.

The rate of bubble nucleation per unit area, \( q \), was also measured. This quantity also remained constant with electrolyte viscosity. The type of electrolyte also made little difference to the results for \( N \) and \( q \).

In order to apply the population balance, estimates for \( N \), \( q \) and the rate constant, \( k \), are needed. Glas et al (1964) shows how \( k \) varies with current. This variation of \( k \) with current is not unexpected after increase in the rate of bubble production was observed with increasing current. This observation could also suggest that \( q \) is a function of current, as seen in equation (15) in section 2. \( N \), being a function of the electrode surface and viscosity needs to be measured specifically for the electrode and electrolyte used under given operating conditions. In order to avoid measuring \( q \), an iterative method is proposed in section 5 whereby \( q \), and the bubble break off diameter can simultaneously be calculated.

The value of the population balance method in analysing bubble growth at gas evolving electrodes is that only one fairly simple experiment needs to be done (see sections 3 and 5). Having established \( N \), \( k \) can be obtained from Glas et al (1964) and then proceeding with the calculation outlined in section 5, a bubble break off diameter can be established. This bubble break
The calculation of mass transfer between electrodes.

In the experiment three parameters were varied: the electrolyte through the cell, the current passed between the electrodes, and the viscosity of the electrolyte. The viscosity of the electrolyte was varied by adding either glycerine or magnesium sulphate. These two substances were chosen because they are chemically very different and did not react in any way at the electrode.

The affect of changing the current (at constant flowrate and viscosity) did not have a significant effect on the size of the bubbles on the electrode. An increase in the current did however increase the number of bubbles produced, and hence the amount of gas produced. The increase in gas production with increasing current is explained by Faraday's Law, but the fact that the bubble sizes remained approximately constant with changes in current would suggest that the bubble break off diameter is not a significant function of current over the range tested. Because the number of bubbles produced increased rather rapidly with current, it was difficult to photograph the cathode under high current conditions, as the bubbles tended to make the solution murky. For this reason the range of currents used was limited.

The flowrate had a small effect on the bubbles growing on the cathode. The bubbles observed on the cathode at high flowrates were smaller than those observed under low flowrate conditions. This effect is more marked in the experiment performed using a low viscosity electrolyte because larger flowrates could be achieved. The reason for the bubbles being smaller w
higher flowrates is that the higher flowrate raises a larger shear stress at the electrode surface. This shear stress then served to dislodge bubbles off the electrode surface prematurely.

The use of glycerine or magnesium sulphate to increase the viscosity of the electrolyte did not appear to have a significant effect. As the viscosity increased over the range used, the mean bubble diameter on surface (based on a volume distribution) decreased by between 25 per cent to 30 per cent, while the mean bubble diameter leaving the surface (the bubble break off diameter) decreased by between 20 per cent to 25 per cent. This decrease in bubble size with increasing viscosity was also observed during the runs in which zinc sulphate was added to the electrolyte to alter the viscosity. As the zinc concentration reached a certain value, the zinc began to plate out onto the cathode. At this point there was a sudden increase in the size of the bubbles produced but again as the viscosity increased beyond this point the bubble sizes again began to decrease. The reason proposed for this sudden jump in bubble size is that as the zinc began to plate out, the electrode surface changed, and so suddenly an essentially different electrode was being used.

The bubble break off diameters observed throughout these experiments were larger by more than a factor of two from those recommended by Stephan (1979). This is probably due to the fact that in this study the bubble break of diameters are based on volume distributions rather than on number distributions.

In conclusion, the population balance provides a means of modelling electrolyte generation of gas. It also allows the bubble break off
diameter to be predicted for use in mass transfer calculations.

The population balance also predicts the distribution of bubble sizes leaving the electrode surface. In using the mean bubble break off diameter in the mass transfer calculations, one is assuming that the bubble size distribution has no effect on the mass transfer at gas evolving electrodes. It is possible, however, that the effect of the large bubbles is far more significant than the effect of the smaller bubbles (and vice versa), and hence the population balance provides a means of predicting the distribution and hence its effect on mass transfer.

The effect of viscosity on the bubble break off diameter was not as marked as was originally anticipated, and hence the conflict between Ault (1975) and Stephan (1979) as pointed out in section 1.4 is not resolved. It was, however, found that the bubble break off diameters measured in this study were larger than those presented by Stephan (1973) for the use in predicting mass transfer coefficients.
7. References


Herder, G., and Iminitoff, M., (1981), "The determination of hydrogen bubble sizes", 4th year Laboratory Project, University of the Witwatersrand, Johannesburg


Appendix 1. Expressions for the Rate of Bubble Growth

Two models for the rate of electrolyte bubble growth are described in detail in this appendix.

1. Darby and Hague (1973)

Darby et al (1973) set about trying to elucidate the controlling rate process which limits the maximum rate at which bubbles are evolved at an electrode. They set up an experiment in which hydrogen bubbles grew from a single nucleation site on the tip of a platinum wire. They initially expected the rate of bubble growth to be analogous to that observed in nucleate boiling, and postulated:

\[
\text{Sh} = \text{constant (Re Sc)}^{1/3}
\]

where

\[
\text{Sh} = \frac{2k_r r}{D} = \text{Sherwood number}
\]

\[
\text{Re} = \frac{2r u c_m}{\mu} = \text{Reynolds number}
\]

\[
\text{Sc} = \frac{c_m}{\rho_m D} = \text{Schmidt number}
\]

\[
k_r = \text{mass transfer coefficient for H}_2
\]

\[r = \text{bubble radius}
\]

\[D = \text{molecular diffusivity}
\]

\[\rho_m = \text{liquid density}\]
\[ \mu = \text{liquid viscosity} \]

and

\[ \mu = \left( \frac{\rho_L \rho_g}{\rho_L - \rho_g} \right)^{0.25} \]

\[ \rho_g = \text{gas density} \]

\[ \gamma = \text{surface tension} \]

Equation (1) predicts the bubble radius to grow in proportion to \( t^{2/3} \), and assumes limiting hydrogen mass transfer.

Darby et al (1973) go on to show that the rate of gas generation at the electrode, \( r_g \), is given by Faraday's Law:

\[ r_g = \frac{I}{nF} \quad (2) \]

where

- \( I \) = total instantaneous current
- \( n \) = number of electrons transferred per Hz molecule
- \( F \) = Faraday's constant.

The rate of mass transfer of dissolved gas from the solution to the bubble, \( r_e \), is:

\[ r_e = k_e A (C_{H_2} - \bar{C}_{H_2}) \quad (3) \]

where

- \( A \) = electrode area
- \( C_{H_2} \) = concentration of dissolved Hz at the electrode
- \( \bar{C}_{H_2} \) = saturation concentration of Hz in equilibrium with partial Hz gas pressure

Finally, the rate of removal of gas from solution by the bubble, \( r_d \), is:
\[ V_b = \frac{3V}{m} \]

\[ \rho_m = \text{molar density of hydrogen} \]
\[ V = \text{bubble volume} \]
\[ t = \text{time}. \]

At steady state, \( V_b = r_t \).

A mass balance on the hydrogen gives:

\[ V_L \frac{\partial C_{H_2}}{\partial t} = r_q - r_b \]

\[ = r_t - r_b = \frac{I}{nF} - \frac{3V}{m} \frac{1}{t} \]

or

\[ V_L \frac{\partial C_{H_2}}{\partial t} = r_q - r_t = \frac{I}{nF} - k_L \lambda(C_{H_2} - \bar{C}_{H_2}) \]

where \( V_L \) = volume of liquid

Now if mass transfer of hydrogen gas to the bubble is limiting (as in the case of the model discussed in section 2 of this appendix), \( k_L \) will be small and there will be a significant build up of dissolved hydrogen in the liquid for a given current. Consequently there will be a difference between the electrode current, which is proportional to \( r \), the rate of gas generation, and the bubble growth rate, corresponding to gas removal.

If mass transfer is not limiting (\( k_L \) large), the generated gas will be transported to the bubble essentially as fast as it is generated. In this case the electrode current and bubble growth rate should be in phase.

The results of Darby et al (1973) show that:

\[ r = 0.15t^{1/3} \]

(7)
This is inconsistent with the predictions of (1), and suggests that some mechanism other than hydrogen mass transfer is limiting. As further evidence of this, they noted that no phase lag between the electrode current and the bubble growth rate was evident.

Darby et al. (1973) went on to apply Faraday's Law:

\[ I(t) = 2F \frac{dV}{dt} \]  

(8)

The current, \( I(t) \), is the instantaneous total current passing through the electrode, and due to fluctuations with time it is written as a function of time. The average current, \( \bar{I} \), was calculated in two ways:

\[ \bar{I} = \frac{1}{t_1} \int_{t_0}^{t_1} I(t) \, dt \]  

(9)

This integral was evaluated by integrating the \( I(t) \) curve numerically.

or

\[ \bar{I} = \frac{2F}{t_1} \frac{V_1}{t_1} \]  

(from Faraday's Law)  

(10)

Here \( \bar{I} \) is calculated by measuring the volume of gas produced, \( V_1 \), in a time \( t_1 \).

The error between the two methods for calculating \( \bar{I} \) was found to be less than 10 per cent.

Now equation (8) can be integrated by replacing \( I(t) \) with \( \bar{I} \), and by writing \( V = \frac{4}{3} \pi r^3 \) to give:

\[ r = \frac{3\bar{I}}{8 \pi F \rho_m} \left( \frac{1}{3} \right)^{1/3} t^{1/3} \]  

(11)
Equation (11) is of the same form as the experimental result of equation (7).

By equating coefficients of equations (7) and (11) and solving for \( \bar{I} \), Darby et al. (1973) found that the calculated value of \( \bar{I} \) was equal to the average value obtained from (9) and (15).

Darby et al. (1973) then go on to show that the rate controlling step is in fact a surface reaction (s→h as atomic hydrogen combining to form molecular hydrogen).

Now \( \bar{I} = \text{bubble diameter} \)

\[
\bar{I} = 2r = \left( \frac{3}{4} \right) \left( \frac{4 \pi}{3} \right)^{1/3}
\]

or

\[
u = \frac{3}{2} \frac{3}{2} \frac{4 \pi}{3} \left( \frac{3}{4} \right)^{1/3} k' t^{3/4}
\]

Assuming the gas behaves ideally:

\[
\rho_m = \frac{p}{R T}
\]

Hence at 25°C and 0.82 atm, \( \rho_m = \frac{0.82 \times 1.01325 	imes 10^5}{8.3143 \ (25+273)} = 33.5 \text{mol/m}^3 \)

\[
k' = \frac{2}{3} \frac{3}{2} \frac{4 \pi}{3} \left( \frac{3}{4} \right)^{1/3} \left( \frac{3}{4} \right)^{3/4}
\]

\[
= 2.22 \times 10^{-3} \ \text{mol/m}^2 \text{s}^{1/4}
\]
2. Scriven (1959)

Scriven (1959) derived a model to describe the growth rate of spherical bubbles growing on an electrode surface in a quiescent liquid of infinite extent. The growth rate is a function of the difference between the pressure within the bubble and the ambient pressure, liquid inertia and viscosity, surface tension and the transport of energy and volatile material through the liquid to the bubble surface (i.e. heat and mass transfer). Scriven (1959) described the growth rate of the bubbles growing on an electrode surface by applying the fundamental equations of fluid dynamics (i.e. the equations of continuity, motion, energy and mass) and then solving simultaneously for the bubble radius as a function of time.

Equation of Continuity

The equation of continuity when written for spherical symmetry and an incompressible fluid can be integrated to give

\[ uR^2 = f(t) \]  

(14)

where

- \( u \) = radial velocity of the liquid being displaced by the growing bubble at a distance \( R \) from the bubble centre
- \( R \) = radial distance
- \( f(t) \) = a function of time.

Since the term \( uR^2 \) is a function of time only, it can be evaluated at any radial position, say, at the bubble surface where \( R = r \). The bubble surface moves with a velocity \( f \), while the liquid immediately adjacent moves with a velocity \( u(r) \). The net velocity causes a mass flow of

\[ 4\pi r^2 u \int f - u(r) \]  

which must equal the rate of vaporization of volatile
The growth rate of the bubbles growing on an electrode surface in a quiescent liquid of infinite extent, described by the fundamental equations of fluid dynamics (i.e. the equation of continuity, motion, energy and mass) and then solving simultaneously for the bubble radius as a function of time.

Equation of Continuity

The equation of continuity for spherical symmetry and an incompressible fluid can be integrated to give

\[ u_R = f(t) \]  

where 

- \( u_R \) is the radial velocity of the liquid being displaced by the growing bubble at a distance \( R \) from the bubble centre
- \( f(t) \) is a function of time.

Since \( u_R \) is a function of time only, it can be evaluated at any instant, say, at the bubble surface where \( R = r \). The bubble grows at a velocity \( \dot{r} \), while the liquid immediately adjacent to the bubble surface has a velocity \( u(r) \). The net velocity causes a mass flow of which must equal the rate of vaporization of volatile
material into the bubble:

\[ 4 \pi r^2 \rho L \left\{ \dot{z} - u(r) \right\} = \frac{\partial}{\partial t} \left( \frac{\partial}{\partial r} \right) \]

where \( \rho = \) vapour density which is assumed constant.

Solving equation (15) for \( u(r) \) gives:

\[ u(r) = k \left[ \frac{dL}{dr} \right] \cdot \frac{1}{r} \]

Hence at the bubble surface, substituting equation (16) we obtain:

\[ uR^2 = cr \]

**Equation of Motion**

Writing the equation of motion in spherical coordinates for an incompressible Newtonian fluid, and assuming no external body force:

\[ \frac{3u}{3t} + u \frac{3u}{3r} = \frac{1}{\rho} \frac{3p}{3r} + \frac{1}{\rho} \frac{33}{3u} \]

where \( p = \) pressure in the moving fluid

\( \nu = \) kinematic viscosity

Substituting for velocity from equation 16 and integrating over the radius from the bubble surface to infinity reduces equation 18 to:

\[ \frac{r^2 - R^2}{2} - \frac{1}{2} \varepsilon \frac{4}{3} \rho \varepsilon \]

where \( \varepsilon = \frac{2r}{3} + \frac{1}{3} \rho \)
Now $p(\infty)$ is just the ambient pressure, $p_\infty$, while $p(r)$ is given by

$$p(r) = P_v + P_l - \frac{\sigma}{r}$$  \hspace{1cm} (30)

where

- $P_v$ = partial pressure of the volatiles in the bubble
- $P_l$ = partial pressure of inert gases in the bubble
- $\sigma$ = surface tension

Now substituting (30) into (19) gives

$$\frac{p_r + P_l - P_\infty - 2\sigma/r}{\frac{\rho T}{\rho_a}} = \frac{1}{2} + \frac{3}{2} \frac{r}{R} + 4 \frac{r^2}{R^2}$$  \hspace{1cm} (21)

The partial pressure of the volatile gas, $p_v$, is specified by assuming a thermodynamic equilibrium between vapor and liquid at the bubble surface. Hence it depends on temperature, which in turn depends on the rates of mass and energy transfer.

**Equation of Energy**

Writing the equation of energy for spherical symmetry, incompressible fluid, negligible viscous dissipation, no energy fluxes other than ordinary conduction, and constant thermal properties:

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial R} = \frac{1}{\rho a} \left( \frac{3}{3R^2} + \frac{2}{R} \right) + \frac{Q}{\rho_v C_{p_L}}$$  \hspace{1cm} (22)

where

- $T$ = temperature at a point $R$ from the bubble centre
- $a$ = thermal diffusivity
- $Q$ = “heat generation” per unit volume
- $C_{p_L}$ = specific heat of the liquid.
Substituting (17) into (22) gives:

\[
\frac{\partial T}{\partial t} = \alpha \left[ \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} - \frac{\kappa r H}{\rho c_p L} \right]
\]

Equation of Mass

Writing the equation of mass for a two component system in which chemical reaction effects are absent: spherical symmetry, constant mass density, no mass fluxes other than ordinary diffusion, and constant mass diffusivity:

\[
\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{R} \frac{\partial C}{\partial r} \right)
\]

where

- \( C \) = mass concentration of volatile species in solution
- \( D \) = mass diffusivity

Substituting equation (17) into (24) gives

\[
\frac{\partial C}{\partial t} = D \left[ \frac{1}{3 R^2} R^2 \frac{\partial C}{\partial R} + \frac{2}{R} \frac{\partial C}{\partial r} \right] - \frac{\kappa C}{\rho c_p L}
\]

At this point there are three equations (equations 21, 23 and 25) in three unknowns \((r, t, C, T)\). Hence, from this system of equations, \( r \) can be solved for in terms of \( t \).

Initial Conditions

The initial conditions for equations (21), (23) and (25) are

\[
\dot{r}(0) = 0
\]

i.e. the initial bubble growth velocity is zero.
i.e. the liquid is initially of uniform temperature and composition.

Scriven [359] also assumes that initially the bubble radius is some size which is equal to the equilibrium radius at the initial conditions

\[ r(0) = \frac{2g}{P_{vo} + P_{io} - P_e} \]  

(29)

where

- \( P_{vo} \) = partial pressure of volatile gas at time \( t = 0 \)
- \( P_{io} \) = partial pressure of inert gas at time \( t = 0 \)

Boundary Conditions at Infinity

If the "heat generated" term in equation (23) is independent of position at large distances then

\[ T_m(t) = T_0 + \frac{1}{\rho c_{PL}} \int_0^t Q(\sigma, t') \, dt' \]  

(30)

The concentration of the dissolved gas at a large distance from the electrode is assumed constant at \( T_m \), hence

\[ C(\sigma, t) = C_m \]  

(31)

Boundary Conditions at the Bubble Surface

The boundary conditions at the bubble surface are obtained from mass and energy balances over the bubble surface. A mass balance, much like one used in equation (15), but now including a diffusion term gives:
\[ m \rho \dot{V} = C(r,t) \left\{ \dot{r} - u(r) \right\} + D \frac{\partial C}{\partial r} \left. \right|_{R=r} + C(r,t) \left\{ (1 - \kappa)F + D \frac{\rho}{R} \right\} \]

where \( m \) = mass fraction of volatile gas in the bubble.

The energy balance after neglecting the kinetic energy terms, changes in vapour density, surface energy and internal energy, and heat of mixing reduces to:

\[ \rho \dot{E} \left\{ L + C \rho |T| \right\} = \beta L C_{FL} \left\{ T(r,v) - T_{0} \right\} \left( 1 - \kappa \right) \frac{\rho}{R} + k_{e} \left( \frac{\rho}{R} \right) \frac{\partial T}{\partial r} \]

where \( \tilde{L} \) = latent heat of vaporization
\( k_{e} \) = thermal conductivity

The partial pressure of the volatile gases is obtained assuming thermodynamic equilibrium between the liquid and gas phases.

At this point Scriven (1959) proceeds to make some simplifying assumptions to aid the solution:

(a) Viscous terms in equation (21) are neglected. This assumption is justified for liquids near their boiling point. During the early stages of growth this assumption is poor.

(b) Inertia and surface tension terms in equation (10) are neglected since they are only significant in the initial expansion.

(c) \( p_{i} \) is neglected in equation (10) - i.e. no inert gases are assumed to be present.
(d) The "heat generated" terms in equations (23) and (30) are neglected.

Scriven (1959) then proceeds to solve the system of equations, and shows for bubble growth controlled by mass transfer (e.g., electrolytic bubble growth):

\[ r = 28 \sqrt{Dt} \]  

where \( \delta \), the growth constant, is defined as

\[ \delta \frac{C_L - C_{sat}}{C_{sat}} = \frac{1}{\delta^2 + \gamma} - \frac{1}{\delta^2} \cdot \frac{1}{\gamma} \cdot \int_0^\infty \frac{\exp(-\alpha^2)}{\alpha^3} \, d\alpha \]

where \( C_{sat} \) = saturation concentration of volatile gas in solution.

The function \( \delta \) can be evaluated, and Scriven (1959) presents a table where by the value of \( \delta \) for a given \( \beta \) and \( c \) can be obtained.

Hence \( r = t^{1/2} \)

or \( t = 2r = 2kt^{1/2} \)  

\( k \) = rate constant for bubble growth

\( l \) = bubble diameter

and \( \frac{dl}{dt} = kt^{1/2} \)

Westerheide et al (1961) and Glas et al (1964) found the bubble radius, \( r \), to be proportional to \( t^{1/6} \) experimentally.

In his solution, Scriven (1959) assumed that the bubble was of a finite size at time \( t = 0 \) although \( R = 0 \) at \( t = 0 \). Because of this assumption, Scriven's model does not describe the rapid initial growth observed by both Westerheide et al (1961) and Glas et al (1964) before the asymptotic
growth predicted by the model.

Glas et al (1964) investigated this initial growth period, and found that its duration was of the order of 0.0006 seconds. They found that although the asymptotic growth was independent of the type of electrode used, the rapid initial growth was dependent on the type of metal. The reason proposed for this by Glas et al (1964) was that during this initial period surface tension forces were significant. The harder metal electrodes (such as nickel) produced smoother surfaces, and hence fewer nucleation sites. So the harder metals experienced a longer initial wait before bubbles started to form. This gives rise to large local supersaturation which in turn causes the very rapid early growth phase.

From (34) and (36) it is clear that \( k = 3 \gamma \). Table A 1.1 below shows the values of \( k \) measured by Westerheide et al (1961) and Glas et al (1964).

Table A 1.1 Values of \( k \) measured by Westerheide et al (1961) and Glas et al (1964)

<table>
<thead>
<tr>
<th>Run</th>
<th>( k ) (m s(^{-1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 ) on Pt 0.083 A/cm(^3)</td>
<td>4.918 \times 10^{-5}</td>
</tr>
<tr>
<td>( H_2 ) on Pt 0.0392 A/cm(^2)</td>
<td>2.821 \times 10^{-5}</td>
</tr>
<tr>
<td>( H_2 ) on Ni 0.084 A/cm(^3)</td>
<td>5.303 \times 10^{-5}</td>
</tr>
<tr>
<td>( H_2 ) on Ni 0.034 A/cm(^2)</td>
<td>2.632 \times 10^{-6}</td>
</tr>
<tr>
<td>( H_2 ) on Ni 0.041 A/cm(^2)</td>
<td>3.154 \times 10^{-5}</td>
</tr>
<tr>
<td>( H_2 ) on Ni 0.076 A/cm(^2)</td>
<td>4.296 \times 10^{-6}</td>
</tr>
<tr>
<td>Westerheide et al (1961)</td>
<td>5.800 \times 10^{-5}</td>
</tr>
<tr>
<td>Westerheide et al (1961)</td>
<td>3.795 \times 10^{-5}</td>
</tr>
</tbody>
</table>
growth predicted by the model.

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From (34) and (36) it is clear that $k = S \cdot D$. Table A 1.1 below shows the values of $k$ measured by Westerheide et al (1961) and Glas et al (1964).

### Table A 1.1 Values of $k$ Measured by Westerheide et al (1961) and Glas et al (1964)

<table>
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<tr>
<th>Run</th>
<th>$k$ ($m \cdot s^{-\frac{1}{2}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$ on Pt</td>
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</tr>
</tbody>
</table>
Appendix 2. Density Functions

In section 5 it was mentioned that a functional form was given to the distribution of bubble sizes leaving the electrode surface, $g(\ell)$. From the shape of the measured distribution, it was felt that three possible density functions could describe the shape:

(1) Gamma density function:

$$g(\ell) = \frac{b^{a+1}}{\Gamma(a+1)} \ell^{a} e^{-bl}$$

where

$a > 0$

$b > 0$

and $\Gamma(a+1) = \text{gamma function} = \int_{0}^{\infty} y^{a} e^{-y} dy$.

(2) Beta density function:

$$g(\ell) = A \left( \frac{\ell}{l_{m}} \right)^{n} \left( 1 - \frac{\ell}{l_{m}} \right)^{c-n}$$

where

$\mu = \frac{\ell}{l_{m}} \geq 1$

$$A = \frac{\Gamma(b+c+2)}{\Gamma(b+1) \Gamma(c+1)}$$

(3) Normal density function:
\[ g(\xi) = \frac{1}{\sqrt{2\pi} \sigma} \exp\left\{ -\frac{(\xi - \mu)^2}{2\sigma^2} \right\} \]

where
\[ \mu = \text{mean of the distribution} \]
\[ \sigma = \text{standard deviation of the distribution} \]

It was found that the normal and gamma density functions best fitted the measured size distributions of the bubbles leaving the electrode surface.

The \( n \)th moment of a density function is defined as

\[ \beta_n = \int_{-\infty}^{\infty} t^n g(\xi) d\xi \tag{1} \]

for \( n = 1, 2, 3, \ldots \)

Since \( g(\xi) \) is a density function,

\[ \int_{-\infty}^{\infty} g(\xi) d\xi = 1 \]

Hence the moments of the gamma and normal density functions can be found by evaluating the integral in (1). In both cases the integral can be evaluated analytically.

For the gamma density function it is found that:

\[ \beta_n = \frac{(a+n)(a+n-1) \ldots (a+1)}{\Gamma(a)} \] \( \tag{2} \)

For the normal density function it can be shown that
From the first two moments the parameters of the density function can be evaluated. The first moment of a density function is equal to the mean of the distribution, while the second moment is equal to the sum of the variance and the square of the mean of the distribution. This is evident from the first two moments of the normal distribution. For the gamma density function, $\beta_1$ and $\beta_2$ can be evaluated as described above. Equation (2) then gives

$$\beta_1 = \frac{a + 1}{b}$$  \hspace{2cm} (4a)$$

$$\beta_2 = \frac{(a + 2)(a + 1)}{b^2}$$  \hspace{2cm} (4b)$$

Solving (4a) and (4b) simultaneously gives

$$a = \frac{2\beta_1 \beta_2 - \beta_2}{\beta_2 - \beta_1}$$  \hspace{2cm} (5a)$$

$$b = \left(\frac{2\beta_1}{\beta_2 - \beta_1}\right)^{\frac{1}{\beta_1}}$$  \hspace{2cm} (5b)$$

Using these values of $a$ and $b$ the $n^{th}$ moment of the gamma density function can be evaluated.
Appendix: Bubble Diameter on the Electrode Surface

A method of taking photographs of the bubbles on the electrode surface is described. These photographs were taken through a sapphire window and then enlarged in the dark room. In order to establish the magnification achieved by the process, a ruler was placed up against the glass window after each run and photographs were taken under the same conditions as were used in the experiment (i.e., using the same magnification on the microscope and through the same electrolyte). This photograph of the ruler was then developed and printed under the same conditions as the photographs of the bubbles. In this way a means of scaling the bubble diameters measured from the photographs was obtained.

The actual measuring of the bubble diameters was done with the aid of a Hewlett Packard model 10 desktop computer and a Hewlett Packard HP 7470 A plotter. A digitizing sight was fitted into the plotter pen holder, and by moving the sight from one edge of a bubble to the other, the bubble diameter could be measured in terms of plotter units. To convert the measurements from plotter units into microns, the two edge points on the millimeter scale on the photograph of the ruler were digitized first, and hence the length of the one millimeter scale was known in plotter units; hence

\[
\frac{\text{bubble diameter in microns}}{\text{millimeter scale in plotter units}} = 1000
\]
The factor of 1000 converts the measurement from millimeters to microns.

The program presented at the end of this appendix allows the user to measure the millimeter scale as many times as required, and an average measurement was then taken (subroutine "Scale"). The user can then proceed to measure the bubble diameters on the photographs (subroutine "Measure"). Having completed the measurements the data is stored on disc for future reference. The mean and standard deviation of the bubble diameters is calculated in lines 1270 - 1360. The data is then sorted into size intervals and a histogram of the size distribution is drawn in subroutine "Plot" on lines 2930. A normal distribution curve based on the measured mean and standard deviation is superimposed on the histogram (lines 2960 - 2990). The program also allows the user to read in the data at a later stage (subroutine "Read") in order to reproduce the calculations and plot.
I program to measure bubble diameter and to sort them into sizes.

intervals so that a histogram may be drawn.

OPTION BASE 1
46 DIM Basin(200),Data(200),Dummy(200),Interval(200)
54 CONTROL 1,12; 1 SWITCH OFF THE KEY LABELS
64 GRAPHICS OFF:
78 OUTPUT 2 USING "#","#" CLEAR THE SCREEN
80 LINPUT "Has the data been previously stored ?",Y
90 IF LCP$(Y$(1,1))="" THEN IF yes, then skip the measuring routine
100 GOSUB Read
110 GOTO 116
120 END IF

INPUT THE VISCOSITY, CURRENT & FLOWRATE USED:

140 LINPUT "What was the viscosity (cP)?",Viscosity$
150 LINPUT "What was the current (Amps)?",Current$
160 LINPUT "What was the flowrate (l/min)?",Flow$

Set up measuring routine

180 PLOTTER IS 785,"HPCL"
190 PRINTER IS 1
200 Control 1,12,1
230 OUTPUT 2,"SCRATCH KEY$" CLEAR the present keys
240 OUTPUT 2 USING "#","#" CLEAR the screen
250 OFF KEY
260 GRAPHICS OFF
270 ON KEY 5 LABEL "Measure" GOSUB Measure GOTO MEASURING ROUTINE
280 ON KEY 9 LABEL "Scale" GOSUB Scale GOTO ROUTINE TO MEASURE SCALE
290 CONTROL 1,12,1
310 GOTO 144
310 Finished; ! When finished 'EDITKEYS' are reloaded

320 MASS STORAGE IS ":HP9121,700,1"
330 LOAD KEY 'EDITKEYS'
340 MASS STORAGE IS ":HP9121,700,1"
350 CONTROL 1,12,1 ! SWITCH ON KEY LABELS
360 GRAPHICS OFF
370 OUTPUT 2 USING "+",1;"XX" ! CLEAR THE SCREEN
380 STOP !
Scale routine which assumes the scale used is a measure of mm.
The scale can be measured any number of times. An average scale is then calculated.

OFF KEY 9 ! DEACTIVATE KEY 9
I=1
Scale=0
PRINT TAB(1,1),"Enter the scale as many times as you want."
PRINT "When finished press 'ENTER' on the plotter twice at the same point."
Start:
DISP "Enter left hand point of mm scale."
Digitize(Xscale1,Yscale1) ! DIGITIZE THE ONE SIDE OF THE SCALE
DISP "Enter right hand side of mm scale."
Digitize(Xscale2,Yscale2) ! DIGITIZE THE OTHER SIDE OF THE SCALE
DISP **
Xscale=ABS(Xscale-Yscale)
Yscale=ABS(Yscale-Yscale)
IF NOT Xscale AND NOT Yscale THEN Leap (FINISHED MEASURING)
IF NOT Yscale THEN
Scale=Yscale+Scale
PRINT TAB(1,1),"Scale = ";Yscale
ELSE
Scale=Xscale+Scale
PRINT TAB(1,1),"Scale = ";Xscale
END IF
I=I+1
GOTO Start ! Measure the scale again.

Leap:I=I-1
Scale=Scale/I ! CALCULATE THE AVERAGE SCALE
Flags ! Set Flag to show that scale has been entered
RETURN
Measure: Routine to measure bubble diameter

IF NOT Flag THEN  ' Check to see if scale has been set
BEEP 500, .8
DISP "ENTER SCALE FIRST"
WAIT 1.5
RETURN

EMD IF
DF KEY 5  ' DEACTIVATE KEY 5
CONTROL 1,12;1  ' SWITCH OFF THE KEY LABELS
OUTPUT 2 USING "#.#","k"  ' CLEAR THE SCREEN

Next:PRINT TAB(1,1),"When finished press 'ENTER' to plot twice at the same point."
DISP "POSITION PEN ON ONE SIDE OF THE BUBBLE & PRESS 'ENTER' ON THE PLOTTER"
Digitize(Left,Right)  ' DIGITIZE ONE SIDE OF THE BUBBLE
DISP "POSITION PEN ON THE OTHER SIDE OF THE BUBBLE & PRESS 'ENTER' ON THE PLOTTER"
Digitize(Left,Right)  ' DIGITIZE THE OTHER SIDE OF THE BUBBLE
X=ABS(Right-Left)
Y=ABS(Right-Left)

IF NOT X AND NOT Y THEN  ' Check to see if user is finished measuring
N=Count-1
REDIM Bubs(,N)
GOSUB Store  ' If finished then store the data
GOTO Start  ' and then proceed with the analysis.

END IF

IF NOT Y THEN
Bubs(Count)=Y
GOTO Loop

END IF

GOSUB Loop

PRINT TABX(1,1),';SCALES...';
BEEP 501, .3
GOTO Next

PRINT USING "#.#",Bubs(Count)
PRINT IMAGE "The last bubble size was ",Bubs(Count)," microns"
Count=Count+1
GOTO Next

END IF

 Else  
Can only accept a measurement in the X or Y direction
PRINT TAB(1,1),"OOPS
BAD DATA"
BEEP 500, .8
GOTO Next

EMD IF

Bubs(Count)=Bubs(Count+1)/300/Scale  ' Convert measurement to microns
PRINT TAB(1,1),"Number of bubbles measured = ",Count
PRINT USING "#.#",Bubs(Count)
PRINT IMAGE "The last bubble size was ",Bubs(Count)," microns"
Count=Count+1
GOTO Next

Go to Next to measure next bubble
1100 Stat: Start of statistical analysis of bubble sizes
1118 INPUT "Do you wish to end now and not proceed with the calculations?",Y
1120 IF Y.EQ.1 THEN GOTO Finished
1130 ! Initialising variables
1140 REDIM Data(N)
1150 MAT Data= Bubblesize
1160 GCLEAR
1170 Flag=0
1180 Plotr=3 ! Defines plotter position
1190 G="INTERNAL" ! Defines plotter type
1200 Pprint=0 ! Defines printer position
1210 PRINTER IS Print
1220 PLOTTER IS Plot, P
1230 GCLEAR
1240 QUIT
1250 OUTPUT 2 USING "* K", "* X" ! CLEAR SCREEN
1260 CONTROL 1, 12; 1 ! SWITCH OFF KEY LABELS
1270 ! CALCULATE THE MEAN
1280 Mean=SUM(Data) / Mean=mean bubble diameter
1290 Mean=Mean : N !
1300 ! CALCULATE THE STANDARD DEVIATION
1310 MAT Dummy = Mean - Data
1320 MAT Dummy = Dummy^2
1330 Stddev = SUM(Dummy) / Stddev=standard deviation of bubble diameters
1340 Stddev = SQRT(Stddev/(N-1))
1350 PRINT USING 1368; Mean, Stddev
1360 IMAGE "Mean = " , Mean, " microns", "Standard deviation = " , Stddev, " microns" !
1370 ! DIVIDE DATA INTO INTERVALS
1380 Smallest=MIN(Data()) ! Smallest=smallest bubble diameter
1390 Largest=MAX(Data()) ! Largest =largest bubble diameter
1400 PRINT USING 1410; Largest, Smallest
1410 IMAGE "The largest bubble is " , Largest, " microns", "The smallest bubble is " , Smallest, " microns" !
1420 INTERVAL=INPUT "Enter the number of intervals you require", Div
1430 IF Div<1 OR FRACT(Div)+.5 THEN MAKE SURE INPUT IS 10 AND AN INTEGER
1440 BEEP 500, 1
1450 DISP "THAT IS NOT FUNNY" !
1460 WAIT 2
1470 GOTO 1420
1480 END IF
1490 REDIM Interval(Div)+1, Interval()=number of bubbles in each interval
1500 MAT Interval= ()
1510 Divlen=Largest-Smallest)/Div ! Divlen=length of each interval
1520 ! Loop to place each bubble in its correct interval
1530 FOR I=1 TO N
1540 FOR J=1 TO Div
1550 IF Data(I)<Smallest+I*Divlen AND Data(I)>Smallest+(J-1)*Divlen THEN
1560 INTERVAL[J]=Interval[J]+1
1570 GOTO Skip
1580 END IF
1590 NEXT J
1600 NEXT I
1610 DISP ERROR IN Interval" ! A CHECK IN CASE NOT ALL BUBBLES ARE FOUND
1620 STOP
1630 Skip:NEXT I
Start of statistical analysis of bubble sizes

INPUT "Do you wish to end now and not proceed with the calculations? ",Y
IF UPCYC(T(Y(1),1))="Y" THEN GOTO Finished 

! Initializing variables
  REDIM Data(10)
  MAT Data=- Bobsiz
  GCLEAR
  Flag=0
  Pitr=3 ! Defines plotter position
  PS="*INTERVAL" ! Defines plotter type
  Prtr=1 ! Defines printer position
  PLOTTER IS Pitr,PS
  GCLEAR
  OUTPUT 2 USING *,*,*,"CLEAR SCREEN"
  CONTROL 1,12;1 ! Switch off key labels

CALCULATE THE MEAN
  Mean=SUM(Data) / Mean=mean bubble diameter
  Mean=Mean/1

CALCULATE THE STANDARD DEVIATION
  Stddev=SUM(Data) / Stddev=standard deviation of bubble diameters
  Stddev=SUM(Stddev/(N-1))
  PRTNT USING 135;Mean,Stddev
  IMAGE "Mean = ",000.000," microns","Standard deviation = ",000.000," microns"

DIVIDE DATA INTO INTERVALS
  Smallest=MIN(Data) ! Smallest=smallest bubble diameter
  Largest=MAX(Data) ! Largest=largest bubble diameter
  PRNTNT USING 141;Largest,Smallest
  IMAGE,"The largest bubble is ",000.000," microns","The smallest bubble is ",000.000," microns"
  INTERVAL:INPUT "Enter the number of intervals you require",Div
  IF Div<=0 OR FRAC(T(Div)=0) THEN "MAKE SURE INPUT IS >0 AND AN INTEGER"
  DEEP 500,1
  DISP "THAT IS NOT FUNNY" 
  WAIT 2
  GOTO 1420
END IF
  REDIM Interval(Div)+1 ! Interval()=number of bubbles in each interval
  MAT Interval=(1)
  Divlen=Largest-Smallest)/Div ! Divlen=length of each interval

! Loop to place each bubble in its correct interval
  FOR J=1 TO N
  FOR J=1 TO Div+1
  IF Data(J)<Smallest+Divlen AND Data(J)>Smallest+(J-1)*Divlen THEN
    IF Divlen(J)=Interval(J)+1 THEN 
      SKIP
  END IF
  NEXT J
  DEEP 500,1
  DISP "ERROR IN Interval" ! A CHECK IN CASE NOT ALL BUBBLES ARE FOUND
  STOP
  SKIP
  NEXT J
1648 GSUB Prin$ Go to printing routine
1658 LINPUT "Do you wish to change the number of intervals?",Y
1668 IF UPCS$(Y$1,11))="Y" THEN 1420
1678 IF UPCS$Y$(1,11))="M" THEN
1688 BEEP 500,1
1698 DISP "BE SERIOUS"
1700 WAIT 1
1711 GOTO 1659
1720 ELSE
1730 LINPUT "Do you wish to print this result?",Y
1740 IF UPCS(Y$1,11))="Y" THEN 1780
1750 Prnt$=781
1760 GSUB Print
1770 Prnt$=1
1780 END IF
1790 PRINT 15 Prnt$ 1
1800 MAT Interval=(1/N)*Interval
1810 Top=MAX(Interval(*)) ; Top=size of the largest interval
1820 Top=INT(Top/2)+1/16
1830 GSUB Plot ; Data plotting routine
1840 GOTO Finished ; Go to Finished to end
1850 STOP ;
1870 PRINT! Printing routine to output results
1871 "PRINTER IS Print
1880 IF Printr THEN PRINT CHR$(2)
1890 PRINT USING 1930,Viscosity$,Current$,Flow$
1900 PRINT "Solution viscosity is ",Viscosity$," centipoise "; "Current used was ",Current$," amps "; "The flowrate is ",Flow$," 1/min."
1910 PRINT "The number of points used is ";N
1920 PRINT USING 1930;mean;Stddev
1930 PRINT "Mean bubble diameter = ",mean," microns "; "Standard deviation = ",Stddev," microns"
1940 PRINT USING 1950;Largest;Smallest
1960 PRINT "INTERVAL NUMBER",TAB(21),"INTERVAL RANGE (microns)",TAB(60),"NUMBER OF BUBBLES"
1970 PRINT "---------------",TAB(21),"------------------------",TAB(60),"---------------"
1980 FOR i=1 TO Dimo
1990 Y(i,5)=VAL(INT((Smallest+(i-1)*100)+len(100)/100)
2000 TS(i,0)="--"
2010 IF(i,13)=VAL(INT((Smallest+(i-1)*len(100)/100)
2020 PRINT TAB(3),i,TAB(25),Y(i,5),TAB(70),Interval$)
2030 NEXT i
2040 END
This routine plots a histogram of the bubble diameters on the surface of the electrode, and then draws a normal curve calculated from the mean and standard deviation of the bubble diameters through the histogram. The mean and the standard deviation are also shown on the curve.

2110 PLOTTING ROUTINE

2160 ! This routine plots a histogram of the bubble diameters on the surface of the electrode, and then draws a normal curve calculated from the mean and standard deviation of the bubble diameters through the histogram. The mean and the standard deviation are also shown on the curve.

2110 PLOTTING ROUTINE

2120 ALPHA OFF

2170 GRAPHICS ON

2140 IF Plot=3 THEN CCLEAR ! If the plotter is the screen then clear

2150 IF Plot=3 THEN CCL 2 ! If the plotter isn't the screen then pick up a pen

2160 GRAPHICS OFF

2170 OUTPUT USING "$,K","OK" ! Clear the ALPHA screen

2180 DISP "Put a pen in the plotter and press 'CDM' when ready"

2190 PAUSE

2200 OUTPUT USING "",K

2210 ALPHA OFF

2220 GRAPHICS ON

2230 OUTPUT USING "",K

2240 LINE TYPE 1

2250 WINDOW Smallest-2*Divlen,Largest+Divlen/2,Top

2260 DISPLAY Smallest-2*Divlen,Largest+Divlen/2,Top

2270 LONG 5

2280 CSIZE 1,5

2290 CLIP Smallest,Largest,Top

2300 AXES Divlen,AS,Smallest,Top ! Draw axes

2310 CLIP OFF

2320 ! Draw the histogram

2330 FOR I = 1 TO Divlen

2340 IF Interval(I) = 0 THEN 2370

2350 CLIP Smallest+(I-1)*Divlen,Smallest+Divlen/2,Top

2360 FRAME

2370 NEXT I

2380 CLIP OFF

2390 CSIZE 3,5

2400 LONG 5

2410 ! Label the X axis

2420 FOR I = 1 TO Divlen

2430 MOVE Smallest+Divlen,Top

2440 LABEL USING "DDD,DP",Smallest+Divlen

2450 NEXT I

2460 MOVE (Largest+Smallest)/2,-Top/8

2470 CSIZE 5,5

2480 LABEL "Bubble diameter (microns)"

2490 CSIZE 3,5

2500 ! Label the Y axis

2510 FOR I = 1 TO Top STEP .85

2520 MOVE Smallest-Divlen/4,1

2530 LABEL USING "Z,DD","1

2540 NEXT I

2550 CSIZE 4,5

2560 MOVE Smallest-Divlen,Top/2

2570 LDIR 78

2580 LONG 6
1578 LABEL "Fraction of bubbles"

2640 ' Graph heading
2641 10 LOG S
2642 LDIR 0
2643 CIZE 0.1
2644 MAKE (Largest+Smallest)/2,Top=1.2
2650 FOR I=1 TO LEN(File)
2660 IF File[I,I]="_" THEN /..(I,I)="_"," place ", in the file name
2670 NEXT I
2679 LABEL Files
2681 LINE TYPE 3,1
2682 LDIR 8
2683 LDG 5

3174 ' Label mean and standard deviation
3175 MOVE Mean,8
3176 IDRAW 8,Top
3178 IMOVE -Stddev,8
3179 LINE TYPE 1
3180 CSIZE 2,5
3181 LABEL DHW(124)
3182 MOVE Mean.Stddev,Top
3183 IDRAW .25*Stddev,9
3184 LABEL DHW(124)
3185 MOVE Mean,Top
3186 LDG 4
3187 LABEL "M"
3188 MOVE Mean.Stddev/2,Top
3189 LABEL "G"
3190 MOVE Mean.Stddev/2,Top
3191 LABEL "G"

3190 MOVE Smallest,8
3192 FOR I=Smallest TO Largest STEP 2
3193 Exponent=Int(1+EXP(-((1-Mean)/Stddev)*2/2)/Stddev*SDR(2WP))
3194 DMAX 1,Exponent
3195 NSET 1
3196 IF Pltr=1 THEN 2988
3197 OUTPUT 785;"S" ; Put pen down
3198 IF Flag=1 THEN 3148 ; If Flag is set then end
3199 GRAPHICS OFF
3200 LINPUT "Do you want a hard copy ?","%
3201 IF UPCI(741,1)="Y" THEN 3140 ; If yes then output to plotter
3202 Flag=1
3203 Pltr=705
3204 Pd="MPUL"
3205 ALPHA OFF
3206 GRAPHICS ON
3207 GOTO Plot
3208 END IF
3209 GRAPHICS OFF
3210 LINPUT "Do you wish to make air, changes ?","%
3211 IF UPCI(741,1)="Y" THEN GOTO Interval
3212 IF UPCI(741,1)="N" THEN GOTO 3140
3213 GOTO 3100
3214 RETURN
3150 STORE STORE TOTAL IN DISC

3160 MASS STORAGE IS "HP121,700,1"
3170 LINPUT "What will the file be called?",FILE
3180 CREATE SPACE FILE#,2,1792
3190 ASSIGN FILE TO FILE#
3200 OUTPUT FILE,1,TYPE,Current File's Flows
3210 OUTPUT FILE,2,BSIZE($)
3220 ASSIGN FILE TO 1
3230 RETURN
Read data off disc

MASS STORAGE IS ':H:\121,780,1'

LINPUT "Enter the name of the data file" Files

ASSIGN #File TO Files

ENTER #File,1,In,Viscosity,Current,Flow

REDIM Data(N), Dummy(N)

ENTER #File,2,Data($)

ASSIGN #File TO #

RETURN

STOP

END !
3350 Digitize: subroutine to digitize points on the plotter.

3360 SUB Digitize(X,Y)
3370 "Assignment of I/O path to the plotter"
3380 OUTPUT BP USING "K"; "SP"
3390 "Plotter is ready to digitize a point"
3400 REPEAT
3410 "Loop until the 'ENTER' is pressed on the plotter"
3420 OUTPUT BP USING "K"; "OS"
3430 "Ask plotter if 'ENTER' has been pressed"
3440 ENTER PP;S
3450 "Receive plotter response"
3460 UNTIL BIT(S,2)=B
3470 "Check if 'ENTER' has been pressed"
3480 OUTPUT BP USING "K"; "DD"
3490 "Tells plotter to send its present position"
3500 ENTER PP; X, Y, P
3510 "Enter digitized point (plotter position)"
3520 SUBEND !
Appendix 4  Measuring Viscosity

The viscosity of the electrolytes used was measured using an Ostwalds Viscometer. The method is outlined below.

1. The Ostwalds Viscometer

An Ostwalds Viscometer is essentially a "U" tube which has one limb a capillary (see figure A 4.1). There is a small bulb at the top of the capillary into which a volume of liquid is sucked from the bulb in the other limb. The liquid is then allowed to flow down through the capillary, and the length of time the volume of liquid takes to flow down the capillary is measured.

The flow of liquid through a capillary is described by the Poiseuille equation:

\[ V = \frac{\pi Pr^4 t}{8\nu} \]  

where

- \( V \) = volume of liquid passing through the capillary
- \( r \) = radius of the capillary
- \( t \) = time taken for \( V \) to flow through the capillary
- \( \ell \) = length of the capillary
- \( \nu \) = viscosity of the liquid
- \( P \) = pressure difference due to the hydrostatic head between the two liquid levels.
Figure A4.1 Ostwalds Viscometer
Now \( p = \rho gh \) \hspace{1cm} (2)

where \( \rho \) = density of the liquid
\( h \) = difference in height between the two liquid levels

Combining (1) and (2) and solving for \( u \)

\[ u = \frac{\rho ghr}{3\ell V} \] \hspace{1cm} (3)

For a given viscometer, the term \( \frac{\rho ghr}{3\ell V} \) is constant, and equal to \( k \) say.

Hence (3) becomes

\[ u = k \rho h \] \hspace{1cm} (4)

In order to find \( k \), the viscometer must be calibrated using a liquid of known density and viscosity. Having found \( k \), the viscosity of a liquid whose density is known can easily be measured.

1.1 Calibration of the Ostwald Viscometer

Since density and viscosity are functions of temperature, \( k \) will also be a function of temperature. For this reason it is important to calibrate a viscometer at the temperature at which the viscosities are to be measured. The experiments were performed at approximately 25°C, and so the viscometer was calibrated at this temperature.

Pure water was used to calibrate the viscometer. Perry (1973) gives:

At 25°C \( \mu = 0.904 \times 10^{-4} \) kg/ms
\( \rho = 997.07 \) kg/m\(^3\)
The times for the water to flow through the capillary in nine series of runs are tabulated in Table A 4.1 below.

Table A 4.1: Calibration of Ostwald's Viscometer at 25°C

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>106.8</td>
</tr>
<tr>
<td>2</td>
<td>107.0</td>
</tr>
<tr>
<td>3</td>
<td>107.1</td>
</tr>
<tr>
<td>4</td>
<td>107.2</td>
</tr>
<tr>
<td>5</td>
<td>106.9</td>
</tr>
</tbody>
</table>

The average time of 107.0 s was used. Hence

\[ k = \frac{\mu}{\eta} = \frac{8.904 \times 10^{-3}}{997.07 \times 1.07} \]

\[ k = 8.346 \times 10^{-5} \text{ m}^2/\text{s}^2 \]

2. Measuring the Electrolyte Viscosity

In order to ensure the temperature of the electrolyte remained constant during measurement, the viscometer was suspended in a constant temperature bath. The system was allowed to stand for a while until the electrolyte temperature reached the bath temperature. A temperature of 25°C was chosen because it was found that after the electrolyte had been under the spot lights during the experiment, its temperature was approximately 25°C.

In calculating the density of the solution, the contribution from the sulphuric acid was ignored since it was in such a small quantity (18 ml in 3000 ml). The density of the glycerine/water mixture was calculated
by assuming no volume change on mixing, and hence it is simply the sum of
the mass of water and glycerine divided by the sum of the volumes, i.e.

\[
\frac{m_{H_2O} + m_{glycerine}}{V_{H_2O} + V_{glycerine}}
\]

\[
\frac{V_{H_2O}}{V_{H_2O} + V_{glycerine}}
\]

The density of the magnesium sulphate/water solution was obtained from
tables in the Handbook of Chemistry and Physics (1976).

The time \( t \) was measured several times, and an average was used in
calculating the viscosity.
Appendix 5  Results

In this appendix a complete set of results is presented from all the experiments performed. The results obtained from the photographs of the bubbles on the electrode surface are presented first followed by the results obtained from the movies of the bubbles leaving the electrode surface. The results from the bubbles on the surface which are presented here take the form of a computer print out and histogram from the program presented in appendix 3. The print out gives the electrolyte viscosity, current and flowrate used during the run, as well as the mean and standard deviation of the bubble diameters measured as well as the size of the largest and smallest bubbles measured. The table below this information gives one fraction of bubbles in the size intervals into which the bubbles were sorted. The histogram is a graphical presentation of this table. A normal curve calculated from the mean and standard deviation of the measured distribution is drawn over the histogram. The vertical dotted line denotes the position of the mean bubble diameter, and the bar at the top of the figure denotes plus and minus the standard deviation from the mean. These results are presented in the following order: runs using water/sulphuric acid electrolyte, runs using glycerine in the electrolyte, runs using magnesium sulphate in the electrolyte, runs using zinc sulphate in the electrolyte.
Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
Current used was 1 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 71.079 microns
Standard deviation = 17.59E microns
Largest bubble diameter = 116.397 microns
Smallest bubble diameter = 35.104 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.1 - 44.13</td>
<td>2.8571E-02</td>
</tr>
<tr>
<td>2</td>
<td>44.13 - 53.16</td>
<td>1.2857E-01</td>
</tr>
<tr>
<td>3</td>
<td>53.16 - 62.2</td>
<td>1.7143E-01</td>
</tr>
<tr>
<td>4</td>
<td>62.2 - 71.23</td>
<td>2.2857E-01</td>
</tr>
<tr>
<td>5</td>
<td>71.23 - 80.26</td>
<td>1.8571E-01</td>
</tr>
<tr>
<td>6</td>
<td>80.26 - 89.29</td>
<td>1.0000E-01</td>
</tr>
<tr>
<td>7</td>
<td>89.29 - 98.33</td>
<td>8.5714E-02</td>
</tr>
<tr>
<td>8</td>
<td>98.33 - 107.3</td>
<td>2.8571E-02</td>
</tr>
<tr>
<td>9</td>
<td>107.3 - 116.3</td>
<td>4.2857E-02</td>
</tr>
</tbody>
</table>

Bubble diameter (microns)
Water/sulphuric acid electrolyte

Solution viscosity was 0.7 centipoise
Current used was 1 amp
The flow rate was 2 l/min

Mean bubble diameter = 88.740 microns
Standard deviation = 21.705 microns
Largest bubble diameter = 153.201 microns
Smallest bubble diameter = 46.899 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.89 - 60.18</td>
<td>9.230E-02</td>
</tr>
<tr>
<td>2</td>
<td>60.18 - 73.47</td>
<td>1.769E-01</td>
</tr>
<tr>
<td>3</td>
<td>73.47 - 86.76</td>
<td>2.076E-01</td>
</tr>
<tr>
<td>4</td>
<td>86.76 - 100.0</td>
<td>2.307E-01</td>
</tr>
<tr>
<td>5</td>
<td>100.0 - 113.3</td>
<td>1.846E-01</td>
</tr>
<tr>
<td>6</td>
<td>113.3 - 126.6</td>
<td>6.153E-02</td>
</tr>
<tr>
<td>7</td>
<td>126.6 - 139.9</td>
<td>2.307E-02</td>
</tr>
<tr>
<td>8</td>
<td>139.9 - 153.2</td>
<td>2.307E-02</td>
</tr>
</tbody>
</table>

Fraction of bubbles vs. Bubble diameter (microns)
Water/sulphuric acid electrolyte

Solution viscosity was 0.42 centipoise
Current used was 1 amp
The flowrate was 3.75 l/min

Mean bubble diameter = 84.496 microns
Standard deviation = 20.112 microns
Largest bubble diameter = 134.975 microns
Smallest bubble diameter = 39.991 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.99 - 53.56</td>
<td>3.9604E-02</td>
</tr>
<tr>
<td>2</td>
<td>53.56 - 67.12</td>
<td>1.5842E-01</td>
</tr>
<tr>
<td>3</td>
<td>67.12 - 80.69</td>
<td>2.4752E-01</td>
</tr>
<tr>
<td>4</td>
<td>80.69 - 94.26</td>
<td>2.4752E-01</td>
</tr>
<tr>
<td>5</td>
<td>94.26 - 107.8</td>
<td>1.7822E-01</td>
</tr>
<tr>
<td>6</td>
<td>107.8 - 121.4</td>
<td>7.9208E-02</td>
</tr>
<tr>
<td>7</td>
<td>121.4 - 134.9</td>
<td>4.9505E-02</td>
</tr>
</tbody>
</table>
INTERVAL NUMBERS

<table>
<thead>
<tr>
<th>INTERVAL RANGE (Microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.49 - 66.55</td>
</tr>
<tr>
<td>66.55 - 77.6</td>
</tr>
<tr>
<td>77.6 - 88.65</td>
</tr>
<tr>
<td>88.65 - 99.71</td>
</tr>
<tr>
<td>99.71 - 110.7</td>
</tr>
<tr>
<td>110.7 - 121.8</td>
</tr>
<tr>
<td>121.8 - 132.9</td>
</tr>
</tbody>
</table>

FRACTION OF BUBBLES

<table>
<thead>
<tr>
<th>Fraction of Bubbles</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8095E-02</td>
</tr>
<tr>
<td>6.6667E-02</td>
</tr>
<tr>
<td>4.7617E-02</td>
</tr>
<tr>
<td>3.8095E-02</td>
</tr>
<tr>
<td>2.3910E-01</td>
</tr>
<tr>
<td>1.9048E-01</td>
</tr>
<tr>
<td>2.0000E-01</td>
</tr>
<tr>
<td>1.8095E-01</td>
</tr>
</tbody>
</table>

Solution density was 0.72 centipoise. Current was 1 amp, the cell size was 4 x 4 cm. Reaction was between acid electrolyte and sulphuric acid.

Largest bubble diameter: 1.43 microns
Smallest bubble diameter: 0.497 microns.

Standard deviation: 1.9646 microns.
Solution viscosity was 0.92 centipoise.
Current used was 3 amp.
The flowrate was 2 l/min.

Mean bubble diameter = 73.423 microns
Standard deviation = 22.565 microns
Largest bubble diameter = 180.250 microns
Smallest bubble diameter = 45.177 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.17 - 58.68</td>
<td>3.3333E-02</td>
</tr>
<tr>
<td>2</td>
<td>58.68 - 72.19</td>
<td>1.3829E-01</td>
</tr>
<tr>
<td>3</td>
<td>72.19 - 85.69</td>
<td>2.3589E-01</td>
</tr>
<tr>
<td>4</td>
<td>85.69 - 99.2</td>
<td>1.9444E-01</td>
</tr>
<tr>
<td>5</td>
<td>99.2 - 112.7</td>
<td>1.1667E-01</td>
</tr>
<tr>
<td>6</td>
<td>112.7 - 126.2</td>
<td>3.3333E-02</td>
</tr>
<tr>
<td>7</td>
<td>126.2 - 139.7</td>
<td>1.6667E-02</td>
</tr>
<tr>
<td>8</td>
<td>139.7 - 153.2</td>
<td>1.3333E-02</td>
</tr>
<tr>
<td>9</td>
<td>153.2 - 166.7</td>
<td>1.1111E-02</td>
</tr>
<tr>
<td>10</td>
<td>166.7 - 180.2</td>
<td>5.3333E-03</td>
</tr>
</tbody>
</table>
Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise.
Current used was 3 amp.
The flow rate was 3.75 l/min.

Mean bubble diameter = 84.858 microns
Standard deviation = 19.571 microns
Largest bubble diameter = 156.807 microns
Smallest bubble diameter = 49.873 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49.87 - 60.56</td>
<td>5.3691E-02</td>
</tr>
<tr>
<td>2</td>
<td>60.56 - 71.25</td>
<td>2.0845E-01</td>
</tr>
<tr>
<td>3</td>
<td>71.25 - 81.95</td>
<td>2.214E-01</td>
</tr>
<tr>
<td>4</td>
<td>81.95 - 92.64</td>
<td>2.214E-01</td>
</tr>
<tr>
<td>5</td>
<td>92.64 - 103.3</td>
<td>1.6779E-01</td>
</tr>
<tr>
<td>6</td>
<td>103.3 - 114.0</td>
<td>4.6980E-02</td>
</tr>
<tr>
<td>7</td>
<td>114.0 - 124.7</td>
<td>2.6846E-02</td>
</tr>
<tr>
<td>8</td>
<td>124.7 - 135.4</td>
<td>2.6846E-02</td>
</tr>
<tr>
<td>9</td>
<td>135.4 - 146.1</td>
<td>2.0134E-02</td>
</tr>
<tr>
<td>10</td>
<td>146.1 - 156.8</td>
<td>6.1142E-03</td>
</tr>
</tbody>
</table>
Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
Current used was 3 amp
The flow rate was 4.60 l/min

Mean bubble diameter = 73.748 microns
Standard deviation = 17.984 microns
Largest bubble diameter = 155.535 microns
Smallest bubble diameter = 38.884 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.88 - 50.54</td>
<td>3.5652E-02</td>
</tr>
<tr>
<td>2</td>
<td>50.54 - 62.21</td>
<td>2.5000E-01</td>
</tr>
<tr>
<td>3</td>
<td>62.21 - 73.07</td>
<td>3.2317E-01</td>
</tr>
<tr>
<td>4</td>
<td>73.07 - 85.54</td>
<td>1.7683E-01</td>
</tr>
<tr>
<td>5</td>
<td>85.54 - 97.2</td>
<td>7.9268E-02</td>
</tr>
<tr>
<td>6</td>
<td>97.2 - 108.8</td>
<td>8.5366E-02</td>
</tr>
<tr>
<td>7</td>
<td>108.8 - 120.5</td>
<td>3.0488E-02</td>
</tr>
<tr>
<td>8</td>
<td>120.5 - 132.2</td>
<td>1.2195E-02</td>
</tr>
<tr>
<td>9</td>
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<tr>
<td>10</td>
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<td>6.0976E-03</td>
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</tbody>
</table>

Bubble diameter (microns)
Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
Current used was 5 amp
The flowrate was 2.1/min

Mean bubble diameter = 95.050 microns
Standard deviation = 20.823 microns
Largest bubble diameter = 157.174 microns
Smallest bubble diameter = 49.064 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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</thead>
<tbody>
<tr>
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<td>97.11 - 109.1</td>
<td>2.6786E-01</td>
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<td>1.9491E-02</td>
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Bubble diameter (microns)
Water/sulphuric acid electrolyte

Solution viscosity was 0.02 centipoise
Current used was 5 amp
The flow rate was 3.75 l/min

Mean bubble diameter = 83.670 microns
Standard deviation = 18.970 microns
Largest bubble diameter = 125.839 microns
Smallest bubble diameter = 57.657 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>72.29 - 78.11</td>
<td>2.6534E-01</td>
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<td>4</td>
<td>78.11 - 84.92</td>
<td>2.0652E-01</td>
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<td>84.92 - 91.74</td>
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Bubble diameter (microns)
Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
Current used was 5 amp
The flow rate was 3.75 1/min

Mean bubble diameter = 83.670 microns
Standard deviation = 14.998 microns
Largest bubble diameter = 125.839 microns
Smallest bubble diameter = 57.657 microns

<table>
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<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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<td>5</td>
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<td>91.74 - 98.56</td>
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<td>112.2 - 119.0</td>
<td>2.173E-02</td>
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<td>10</td>
<td>119.0 - 125.8</td>
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</table>

Bubble diameter (microns)
Water/sulphuric acid electrolyte

Solution viscosity was 0.92 centipoise
Current used was 3 amp
The flow rate was 4.50 l/min

Mean bubble diameter = 67.709 microns
Standard deviation = 15.580 microns
Largest bubble diameter = 126.325 microns
Smallest bubble diameter = 43.799 microns

<table>
<thead>
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<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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<td>43.79 - 52.05</td>
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<td>1.9444E-01</td>
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<td>60.3 - 60.55</td>
<td>2.7778E-01</td>
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<td>76.0 - 95.06</td>
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<td>95.06 - 93.31</td>
<td>9.2593E-02</td>
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<td>93.31 - 101.5</td>
<td>3.7037E-02</td>
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<td>101.5 - 109.0</td>
<td>1.8519E-02</td>
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<td>109.0 - 116.0</td>
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<td>10</td>
<td>116.0 - 126.3</td>
<td>9.2593E-03</td>
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Bubble diameter (microns)
**Water/sulphuric acid electrolyte**

Solution viscosity was 0.92 centipoise
Current used was 10 amp
The flowrate was 4.60 l/min

Mean bubble diameter = 66.269 microns
Standard deviation = 17.845 microns
Largest bubble diameter = 140.270 microns
Smallest bubble diameter = 41.714 microns

<table>
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<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE ( Microns )</th>
<th>FRACTION OF BUBBLES</th>
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<td>1</td>
<td>41.71 - 54.03</td>
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<td>6.6667E-02</td>
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<tr>
<td>6</td>
<td>103.3 - 115.6</td>
<td>0.0000E+00</td>
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<td>7</td>
<td>115.6 - 127.9</td>
<td>0.0000E+00</td>
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<td>8</td>
<td>127.9 - 140.2</td>
<td>1.6667E-02</td>
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</tbody>
</table>

![Bar graph showing fraction of bubbles against bubble diameter (microns)](image-url)
Conc. of glycerine = 36.7 kg/m^3

Solution viscosity was 1.00 centipoise
Current used was 1 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 84.935 microns
Standard deviation = 17.525 microns
Largest bubble diameter = 130.776 microns
Smallest bubble diameter = 57.763 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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<tbody>
<tr>
<td>1</td>
<td>57.76 - 66.89</td>
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<td>76.01 - 85.14</td>
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<td>4</td>
<td>85.14 - 94.26</td>
<td>2.4000E-01</td>
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<td>5</td>
<td>94.26 - 103.3</td>
<td>8.0000E-02</td>
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<td>103.3 - 112.5</td>
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<td>7</td>
<td>112.5 - 121.6</td>
<td>2.0000E-02</td>
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<tr>
<td>8</td>
<td>121.6 - 130.7</td>
<td>6.0000E-02</td>
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</tbody>
</table>
Conc. of glycerine = 1.12 kg/m³

Solution viscosity was 1.24 centipoise
Current used was 1 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 81.375 microns
Standard deviation = 20.865 microns
Largest bubble diameter = 134.026 microns
Smallest bubble diameter = 42.396 microns

<table>
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<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
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<tbody>
<tr>
<td>1</td>
<td>42.39 - 51.55</td>
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<td>51.55 - 60.72</td>
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<td>3</td>
<td>60.72 - 69.88</td>
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<td>69.88 - 79.04</td>
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<td>5</td>
<td>79.04 - 88.21</td>
<td>1.408E-01</td>
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<td>88.21 - 97.37</td>
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<td>97.37 - 106.5</td>
<td>9.450E-02</td>
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<td>8</td>
<td>106.5 - 115.7</td>
<td>4.225E-02</td>
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<td>9</td>
<td>115.7 - 124.8</td>
<td>1.408E-02</td>
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<tr>
<td>10</td>
<td>124.8 - 134.0</td>
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</tr>
</tbody>
</table>

Bubble diameter (microns)
Conc. of glycerine = 199 kg/m^3

Solution viscosity was 1.62 centipoise
Current used was 1 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 76.768 microns
Standard deviation = 15.120 microns
Largest bubble diameter = 114.817 microns
Smallest bubble diameter = 44.651 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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<tbody>
<tr>
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<td>44.65 - 52.44</td>
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<td>68.03 - 75.83</td>
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<td>75.83 - 83.63</td>
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<td>83.63 - 91.42</td>
<td>1.2000E-01</td>
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<td>91.42 - 99.22</td>
<td>1.3000E-01</td>
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<td>99.22 - 107.0</td>
<td>4.0000E-02</td>
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<tr>
<td>9</td>
<td>107.0 - 114.8</td>
<td>3.0000E-02</td>
</tr>
</tbody>
</table>

Bubble diameter (microns)
Concentration of glycerine = 5.32 kg/m^3

Water viscosity was 0.001 centipoise
Current used was 1 amp
The flow rate was 2.0 l/min

- Double diameter: 3.386 microns
- Standard deviation: 1.205 microns
- Largest bubble diameter: 110.399 microns
- Smallest bubble diameter: 50.847 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
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<tbody>
<tr>
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<td>67.86 - 76.36</td>
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<td>76.36 - 84.87</td>
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<td>84.87 - 93.38</td>
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<td>93.38 - 101.8</td>
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<td>7</td>
<td>101.8 - 110.3</td>
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</tbody>
</table>

![Bar graph showing bubble diameter distribution](image)

![Distribution curve](image)
Solution viscosity was 2.97 centipoise.
Current used was 1 amp.
The flowrate was 2.0 l/min.

Mean bubble diameter = 72.742 microns
Standard deviation = 12.537 microns
Largest bubble diameter = 108.170 microns
Smallest bubble diameter = 50.633 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLE</th>
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<tbody>
<tr>
<td>1</td>
<td>50.63 - 57.02</td>
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<td>57.02 - 63.41</td>
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<td>82.59 - 88.99</td>
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<td>101.77 - 108.17</td>
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</table>
Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise
Current used was 0.5 amp
The flow rate was 1.18 l/min

Mean bubble diameter = 70.204 microns
Standard deviation = 18.685 microns
Largest bubble diameter = 150.726 microns
Smallest bubble diameter = 39.079 microns

<table>
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<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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<tbody>
<tr>
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<td>39.07 - 50.24</td>
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<td>139.5 - 150.7</td>
<td>1.3245E-02</td>
</tr>
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</table>

![Graph showing distribution of bubble diameters](image)
**Conc. of glycerine** = 529 kg/m³

Solution viscosity was 5.0 centipoise
Current used was 0.5 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 70.550 microns
Standard deviation = 21.278 microns
Largest bubble diameter = 145.712 microns
Smallest bubble diameter = 37.350 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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Bubble diameter (microns)
Conc. of glycerine = 5.79 kg/m³

Solution viscosity was 5.8 centipoise
Current used was 0.5 amp
The flowrate was 2.90 l/min

Mean bubble diameter = 68.398 microns
Standard deviation = 21.149 microns
Largest bubble diameter = 161.889 microns
Smallest bubble diameter = 33.114 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
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<tr>
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<td>61.73 – 76.03</td>
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<td>76.03 – 90.34</td>
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<td>104.6 – 118.9</td>
<td>4.633E-02</td>
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<td>118.9 – 133.2</td>
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<td>8</td>
<td>133.2 – 147.5</td>
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<td>147.5 – 161.8</td>
<td>6.622E-03</td>
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</tbody>
</table>

Bubble diameter (microns)

Fraction of Bubbles
Conc. of glycerine = 579 kg/m³

Solution viscosity was 5.8 centipoise
Current used was 1 amp
The flowrate was 1.18 l/min

Mean bubble diameter = 69.778 microns
Standard deviation = 19.652 microns
Largest bubble diameter = 129.653 microns
Smallest bubble diameter = 37.146 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.14 - 48.7</td>
<td>1.3287E-01</td>
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<tr>
<td>2</td>
<td>48.7 - 60.27</td>
<td>2.0280E-01</td>
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<td>60.27 - 71.83</td>
<td>2.5175E-01</td>
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<td>71.83 - 83.39</td>
<td>2.3378E-01</td>
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<td>5</td>
<td>83.39 - 94.96</td>
<td>6.9930E-02</td>
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<td>94.96 - 106.5</td>
<td>5.5944E-02</td>
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<tr>
<td>7</td>
<td>106.5 - 118.0</td>
<td>3.4945E-02</td>
</tr>
<tr>
<td>8</td>
<td>118.0 - 129.6</td>
<td>2.7972E-02</td>
</tr>
</tbody>
</table>

Bubble diameter (microns)
Solution viscosity was 5.8 centipoise
Current used was 1 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 65.879 microns
Standard deviation = 19.215 microns
Largest bubble diameter = 130.514 microns
Smallest bubble diameter = 32.972 microns

<table>
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<tr>
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<tbody>
<tr>
<td>1</td>
<td>32.97 - 45.16</td>
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<td>2</td>
<td>45.16 - 57.35</td>
<td>2.5000E-01</td>
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<td>3</td>
<td>57.35 - 69.55</td>
<td>2.5611E-01</td>
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<td>4</td>
<td>69.55 - 81.74</td>
<td>1.9231E-01</td>
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<td>5</td>
<td>81.74 - 93.93</td>
<td>9.6154E-02</td>
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<td>93.93 - 106.1</td>
<td>3.0462E-02</td>
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<td>106.1 - 118.3</td>
<td>1.9331E-02</td>
</tr>
<tr>
<td>8</td>
<td>118.3 - 130.5</td>
<td>2.5641E-02</td>
</tr>
</tbody>
</table>

Conc. of glycerine = 579 kg/M3
Conc. of glycerine = 5.29 kg/m^3

Solution viscosity was 5.82 centipoise
Current used was 1 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 68.060 microns
Standard deviation = 16.452 microns
Largest bubble diameter = 123.063 microns
Smallest bubble diameter = 37.011 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.01 - 51.35</td>
<td>1.6901E-01</td>
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<td>2</td>
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<td>3</td>
<td>65.69 - 80.03</td>
<td>2.5352E-01</td>
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<td>4</td>
<td>80.03 - 94.37</td>
<td>1.9718E-01</td>
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<tr>
<td>5</td>
<td>94.37 - 108.7</td>
<td>1.4085E-02</td>
</tr>
<tr>
<td>6</td>
<td>108.7 - 123.0</td>
<td>2.0365E-02</td>
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</tbody>
</table>
Conc. of glycerine = 57.9 kg/m³

Solution viscosity was 5.8 centipoise
Current used was 1 amp
The flowrate was 0.90 l/min

Mean bubble diameter = 67.867 microns
Standard deviation = 17.487 microns
Largest bubble diameter = 128.913 microns
Smallest bubble diameter = 27.778 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.77 - 37.39</td>
<td>1.3245E-02</td>
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<tr>
<td>2</td>
<td>37.89 - 48</td>
<td>1.3907E-01</td>
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<tr>
<td>3</td>
<td>48 - 58.11</td>
<td>2.0530E-01</td>
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<td>4</td>
<td>58.11 - 68.23</td>
<td>2.1054E-01</td>
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<td>5</td>
<td>68.23 - 78.34</td>
<td>1.3907E-01</td>
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<tr>
<td>6</td>
<td>78.34 - 88.45</td>
<td>1.1921E-01</td>
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<tr>
<td>7</td>
<td>88.45 - 98.57</td>
<td>9.9338E-02</td>
</tr>
<tr>
<td>8</td>
<td>98.57 - 108.6</td>
<td>2.6490E-02</td>
</tr>
<tr>
<td>9</td>
<td>108.6 - 118.7</td>
<td>1.9068E-02</td>
</tr>
<tr>
<td>10</td>
<td>118.7 - 128.9</td>
<td>1.9368E-02</td>
</tr>
</tbody>
</table>
**Conc. of glycerine: 579 kg/m^3**

Solution viscosity was 5.8 centipoise  
Current used was 1.5 amp  
The flowrate was 1.18 l/min

**Mean bubble diameter** = 71.110 microns  
**Standard deviation** = 20.606 microns  
**Largest bubble diameter** = 133.272 microns  
**Smallest bubble diameter** = 33.775 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.77 - 44.82</td>
<td>0.2707E-02</td>
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<tr>
<td>2</td>
<td>44.82 - 55.98</td>
<td>1.6541E-01</td>
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<td>3</td>
<td>55.98 - 66.04</td>
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<td>66.04 - 77.11</td>
<td>1.5789E-01</td>
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<td>5</td>
<td>77.11 - 89.05</td>
<td>1.3534E-01</td>
</tr>
<tr>
<td>6</td>
<td>89.05 - 100.1</td>
<td>1.2030E-01</td>
</tr>
<tr>
<td>7</td>
<td>100.1 - 111.1</td>
<td>6.7699E-02</td>
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<tr>
<td>8</td>
<td>111.1 - 122.2</td>
<td>1.5038E-02</td>
</tr>
<tr>
<td>9</td>
<td>122.2 - 133.2</td>
<td>1.5038E-02</td>
</tr>
</tbody>
</table>

**Bubble diameter (microns)**

![Bubble diameter distribution graph](image-url)
Conc. of glycerine = 575 kg/m³

Solution viscosity was 5.8 centipoise
Current used was 1.5 amp
The flow rate was 2.0 l/min

Mean bubble diameter = 69.374 microns
Standard deviation = 20.062 microns
Largest bubble diameter = 129.406 microns
Smallest bubble diameter = 31.574 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>31.57 - 43.8</td>
<td>7.6336E-02</td>
</tr>
<tr>
<td>2</td>
<td>43.8 - 56.03</td>
<td>2.0611E-01</td>
</tr>
<tr>
<td>3</td>
<td>56.03 - 68.26</td>
<td>2.2901E-01</td>
</tr>
<tr>
<td>4</td>
<td>68.26 - 80.49</td>
<td>2.1374E-01</td>
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<td>5</td>
<td>80.49 - 92.71</td>
<td>1.6031E-01</td>
</tr>
<tr>
<td>6</td>
<td>92.71 - 104.9</td>
<td>5.3435E-02</td>
</tr>
<tr>
<td>7</td>
<td>104.9 - 117.1</td>
<td>3.0534E-02</td>
</tr>
<tr>
<td>8</td>
<td>117.1 - 129.4</td>
<td></td>
</tr>
</tbody>
</table>
Solution viscosity was 5.0 centipoise
Current used was 1.5 amp
The flow rate was 2.90 l/min

Mean bubble diameter  = 69.244 microns
Standard deviation  = 22.348 microns
Largest bubble diameter = 150.069 microns
Smallest bubble diameter = 33.961 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.96 - 46.06</td>
<td>1.3740E-01</td>
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<tr>
<td>2</td>
<td>46.06 - 59.76</td>
<td>2.5191E-01</td>
</tr>
<tr>
<td>3</td>
<td>59.76 - 72.66</td>
<td>2.5191E-01</td>
</tr>
<tr>
<td>4</td>
<td>72.66 - 85.56</td>
<td>1.1450E-01</td>
</tr>
<tr>
<td>5</td>
<td>85.56 - 98.46</td>
<td>1.1450E-01</td>
</tr>
<tr>
<td>6</td>
<td>98.46 - 111.3</td>
<td>3.9397E-02</td>
</tr>
<tr>
<td>7</td>
<td>111.3 - 124.2</td>
<td>3.0534E-02</td>
</tr>
<tr>
<td>8</td>
<td>124.2 - 137.1</td>
<td>7.6336E-03</td>
</tr>
<tr>
<td>9</td>
<td>137.1 - 150.0</td>
<td>7.6336E-03</td>
</tr>
</tbody>
</table>
Conc. of my sulphate = 10 kg/m³

Solution viscosity was 1.02 centipoise.
Current used was 1.0 amp.
The flowrate was 0.1/min.

Mean bubble diameter = 72.627 microns
Standard deviation = 15.636 microns
Largest bubble diameter = 100.216 microns
Smallest bubble diameter = 40.639 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.63 - 48.83</td>
<td>6.3291E-02</td>
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<tr>
<td>2</td>
<td>48.83 - 57.03</td>
<td>1.1372E-01</td>
</tr>
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<td>3</td>
<td>57.03 - 65.23</td>
<td>1.2658E-01</td>
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<td>65.23 - 73.42</td>
<td>2.5316E-01</td>
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<td>73.42 - 81.62</td>
<td>1.5190E-01</td>
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<td>6</td>
<td>81.62 - 89.87</td>
<td>1.3924E-01</td>
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<tr>
<td>7</td>
<td>89.82 - 98.01</td>
<td>6.3291E-02</td>
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<tr>
<td>8</td>
<td>98.01 -</td>
<td>9.6608E-02</td>
</tr>
</tbody>
</table>

Bubble diameter (microns)
Solution viscosity was 2.07 centipoise
Current used was 1.0 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 71.567 microns
Standard deviation = 14.286 microns
Largest bubble diameter = 113.904 microns
Smallest bubble diameter = 42.426 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.42 - 52.63</td>
<td>1.2766E-1</td>
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<tr>
<td>2</td>
<td>52.63 - 62.81</td>
<td>2.7660E-1</td>
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<td>3</td>
<td>62.84 - 73.05</td>
<td>5.5322E-1</td>
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<td>4</td>
<td>73.05 - 83.27</td>
<td>7.7021E-1</td>
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<td>5</td>
<td>83.27 - 93.48</td>
<td>1.0000E+0</td>
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<tr>
<td>6</td>
<td>93.48 - 103.6</td>
<td>4.2537E-2</td>
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<tr>
<td>7</td>
<td>103.6 - 113.8</td>
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</tr>
</tbody>
</table>

Bubble diameter (microns)

Fraction of Bubbles
Solution viscosity was 2.54 centipoise
Current used was 1.0 amp
The flowrate was 2.0 l/min

Mean bubble diameter = 67.870 microns
Standard deviation = 11.261 microns
Largest bubble diameter = 92.552 microns
Smallest bubble diameter = 38.218 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.21 - 47.27</td>
<td>2.0833E-02</td>
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<td>2</td>
<td>47.27 - 56.32</td>
<td>1.0750E-01</td>
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<td>3</td>
<td>56.32 - 65.38</td>
<td>6.6667E-01</td>
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<tr>
<td>4</td>
<td>65.38 - 74.44</td>
<td>3.1250E-01</td>
</tr>
<tr>
<td>5</td>
<td>74.44 - 83.49</td>
<td>2.5000E-01</td>
</tr>
<tr>
<td>6</td>
<td>83.49 - 92.55</td>
<td>6.2500E-02</td>
</tr>
</tbody>
</table>
Solution viscosity was 3.17 centipoise
Current used was 1.0 amp
The flowrate was 2.00 l/min

Mean bubble diameter = 81.838 microns
Standard deviation = 18.905 microns
Largest bubble diameter = 156.160 microns
Smallest bubble diameter = 48.300 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>101.2 - 114.9</td>
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<td>128.7 - 142.4</td>
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<tr>
<td>8</td>
<td>142.4 - 156.1</td>
<td>3.3333E-03</td>
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</tbody>
</table>

Conc. of Mg sulphate = 4.70 kg/m^2.5
Concentration of zinc sulphate = 4.2 kg/m³

Solution viscosity was 0.95 centipoise
Current used was 1.0 amp
The flowrate was 2.00 l/min

Mean bubble diameter = 83.896 microns
Standard deviation = 19.350 microns
Largest bubble diameter = 146.850 microns
Smallest bubble diameter = 52.576 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52.57 - 63.05</td>
<td>1.1494E-01</td>
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<td>73.52 - 84</td>
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<td>4</td>
<td>84 - 94.47</td>
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<td>94.47 - 104.9</td>
<td>6.8966E-02</td>
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<td>104.9 - 115.4</td>
<td>2.2999E-02</td>
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<td>115.4 - 125.9</td>
<td>1.1494E-02</td>
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<td>125.9 - 136.3</td>
<td>3.4483E-02</td>
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<tr>
<td>9</td>
<td>136.3 - 146.8</td>
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</tr>
</tbody>
</table>

Bubble diameter (microns)
Solution viscosity was 1.06 centipoise
Current used was 1.0 amp
The flowrate was 2.00 l/min

Mean bubble diameter = 74.626 microns
Standard deviation = 13.893 microns
Largest bubble diameter = 106.594 microns
Smallest bubble diameter = 37.940 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
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<tbody>
<tr>
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<td>37.94 - 44.8</td>
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<td>51.67 - 58.53</td>
<td>9.9765E-02</td>
</tr>
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<td>4</td>
<td>58.53 - 65.4</td>
<td>8.6420E-02</td>
</tr>
<tr>
<td>5</td>
<td>65.4 - 72.26</td>
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<td>72.26 - 79.13</td>
<td>2.2222E-01</td>
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<td>7</td>
<td>79.13 - 85.99</td>
<td>1.8519E-01</td>
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<td>85.99 - 92.86</td>
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<td>92.86 - 99.72</td>
<td>6.1728E-02</td>
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<td>10</td>
<td>99.72 - 106.5</td>
<td>3.7037E-02</td>
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</tbody>
</table>
Conc. of zinc sulphate = 164 kg/m^3

Solution viscosity was 1.14 centipoise
Current used was 1.0 amp
The flow rate was 2.00 l/min

Mean bubble diameter = 71.546 microns
Standard deviation = 12.773 microns
Largest bubble diameter = 112.314 microns
Smallest bubble diameter = 46.459 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (Microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.45 - 54.69</td>
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<td>2</td>
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<td>2.0000E-01</td>
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<tr>
<td>3</td>
<td>62.92 - 71.15</td>
<td>2.8333E-01</td>
</tr>
<tr>
<td>4</td>
<td>71.15 - 79.38</td>
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<td>5</td>
<td>79.38 - 87.61</td>
<td>1.5000E-01</td>
</tr>
<tr>
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<td>87.61 - 95.85</td>
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<td>95.85 - 104.00</td>
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<tr>
<td>8</td>
<td>104.0 - 112.3</td>
<td>1.6667E-02</td>
</tr>
</tbody>
</table>

![Bubble diameter distribution graph](image)
Solution viscosity was 2.2 centipoise
Current used was 1.0 amp
The flow rate was 2.00 l/min

Mean bubble diameter = 73.935 microns
Standard deviation = 15.559 microns
Largest bubble diameter = 139.693 microns
Smallest bubble diameter = 48.748 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.74 - 57.01</td>
<td>1.4407E-01</td>
</tr>
<tr>
<td>2</td>
<td>57.01 - 65.20</td>
<td>1.7797E-01</td>
</tr>
<tr>
<td>3</td>
<td>65.20 - 73.55</td>
<td>2.0342E-01</td>
</tr>
<tr>
<td>4</td>
<td>73.55 - 81.81</td>
<td>1.7727E-01</td>
</tr>
<tr>
<td>5</td>
<td>81.81 - 90.00</td>
<td>1.1842E-01</td>
</tr>
<tr>
<td>6</td>
<td>90.00 - 98.35</td>
<td>1.0169E-01</td>
</tr>
<tr>
<td>7</td>
<td>98.35 - 106.6</td>
<td>4.2373E-02</td>
</tr>
<tr>
<td>8</td>
<td>106.6 - 114.8</td>
<td>0.0000E+00</td>
</tr>
<tr>
<td>9</td>
<td>114.8 - 123.1</td>
<td>8.4746E-03</td>
</tr>
<tr>
<td>10</td>
<td>123.1 - 131.4</td>
<td>0.0000E+00</td>
</tr>
<tr>
<td>11</td>
<td>131.4 - 139.6</td>
<td>9.4746E-03</td>
</tr>
</tbody>
</table>

Bubble diameter (microns)
Conc. of zinc sulphate = 50% kg/m^3

Solution viscosity was 2.5 centipoise
Current used was 1.0 amp
The flowrate was 2.00 1/min

Mean bubble diameter = 73.104 microns
Standard deviation = 14.743 microns
Largest bubble diameter = 101.664 microns
Smallest bubble diameter = 51.732 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF Bubbles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51.73 - 61.71</td>
<td>2.5000E-01</td>
</tr>
<tr>
<td>2</td>
<td>61.71 - 71.7</td>
<td>2.5000E-01</td>
</tr>
<tr>
<td>3</td>
<td>71.7 - 81.69</td>
<td>2.5000E-01</td>
</tr>
<tr>
<td>4</td>
<td>81.69 - 91.67</td>
<td>1.2500E-01</td>
</tr>
<tr>
<td>5</td>
<td>91.67 - 101.6</td>
<td>1.2500E-01</td>
</tr>
</tbody>
</table>

![Bubble diameter distribution graph](graph.png)
The results obtained from measuring the bubbles leaving the electrode surface are tabulated in Table A 5.1 below. These results were all obtained using a flowrate of 2.00 l/min and a current of 1.0 A.

### Table A 5.1 Measurements of Bubble Sizes Leaving the Surface

<table>
<thead>
<tr>
<th>Concentration of glycerine or MgSO₄ (kg/m³)</th>
<th>Viscosity (cP)</th>
<th>Mean Bubble Diameter (µm)</th>
<th>Standard Deviation of Bubble Diameters (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>0.92</td>
<td>127</td>
<td>37</td>
</tr>
<tr>
<td>36.7 kg/m³ glycerine</td>
<td>1.00</td>
<td>112</td>
<td>40</td>
</tr>
<tr>
<td>36.7 kg/m³ glycerine</td>
<td>1.50</td>
<td>95</td>
<td>41</td>
</tr>
<tr>
<td>332 kg/m³ glycerine</td>
<td>2.40</td>
<td>90</td>
<td>33</td>
</tr>
<tr>
<td>386 kg/m³ glycerine</td>
<td>3.00</td>
<td>89</td>
<td>33</td>
</tr>
<tr>
<td>150 kg/m³ MgSO₄</td>
<td>1.44</td>
<td>114</td>
<td>40</td>
</tr>
<tr>
<td>280 kg/m³ MgSO₄</td>
<td>2.07</td>
<td>105</td>
<td>41</td>
</tr>
<tr>
<td>350 kg/m³ MgSO₄</td>
<td>2.54</td>
<td>99</td>
<td>31</td>
</tr>
</tbody>
</table>

Histograms showing the distribution of the above runs are now presented. When results are available from the runs measuring bubble sizes on the electrode surface, the two distributions are superimposed on the same set of axes. The bold bars represent the bubbles leaving the surface while the hatched bars represent the bubbles on the surface.
**Conc. of zinc sulphate** = 0.63 kg/m³

Solution viscosity was 5.0 centipoise
Current used was 1.0 amp
The flowrate was 2.00 l/min

Mean bubble diameter = 67.498 microns
Standard deviation = 6.629 microns
Largest bubble diameter = 80.182 microns
Smallest bubble diameter = 52.392 microns

<table>
<thead>
<tr>
<th>INTERVAL NUMBER</th>
<th>INTERVAL RANGE (microns)</th>
<th>FRACTION OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52.39 - 57.94</td>
<td>1.0526E-01</td>
</tr>
<tr>
<td>2</td>
<td>57.94 - 63.5</td>
<td>1.5789E-01</td>
</tr>
<tr>
<td>3</td>
<td>63.5 - 69.06</td>
<td>3.6843E-01</td>
</tr>
<tr>
<td>4</td>
<td>69.06 - 74.62</td>
<td>2.6316E-01</td>
</tr>
<tr>
<td>5</td>
<td>74.62 - 80.18</td>
<td>1.0526E-01</td>
</tr>
</tbody>
</table>

![Graph of bubble diameter distribution](image-url)
Fraction of Bubbles

Bubble Diameter (microns)
Fraction Of Bubbles

Bubble Diameter (microns)
Appendix 6  Measuring the Current Density

Kasper (1940) showed that the current distribution over a plane electrode, when the opposing electrode is a line electrode is:

\[ i = \frac{-a \cdot \frac{I}{2\pi r}}{r^2} \]

where
- \( i \) = the current density on the plane electrode, a distance \( r \) from the line electrode
- \( a \) = perpendicular distance between the line and plane electrodes
- \( \frac{I}{2\pi} \) = current per unit length of the line electrode.

Figure A 6.1 is a pictorial representation of the system when viewed from above.

Figure A 6.1  The Line and Plane Electrode System described by Equation 1
Inherent in equation (1) is the assumption that the current density does not vary in the direction parallel to the line electrode.

For the system used in the experiments it was assumed that because the anode was so narrow compared to the cathode, the current densities could be calculated by equation (1). For the experiments:

\[ a = 33 \text{ mm} \]

length of the anode = length of line electrode = 88 mm

\[ r = \text{position where photographs were taken, relative to the anode} = 60 \text{ mm} \]

Hence

\[ i = \frac{33 \times 10^{-3}}{88 \times 10^{-3}} \frac{1}{r} \]

\[ i = 33 \frac{1}{I} \text{ A/m}^2 \]

where \( I \) = measured current.
Appendix 7  Solving the Population Balance

In the analysis section, section 5, it was shown that the population balance reduces to

\[ q_n = \frac{n2 \lambda}{\pi zF_p} \int_{\tilde{\ell}}^{\infty} \tilde{\ell}^{n-2} f(\tilde{\ell}) d\tilde{\ell} \]  \hspace{1cm} (1a)

or

\[ q_n = \frac{n2 \lambda}{\pi zF_p} \int_{\tilde{\ell}}^{\infty} \tilde{\ell}^{n-3} f(\tilde{\ell}) d\tilde{\ell} \]  \hspace{1cm} (1b)

Depending on whether the rate of bubble growth is taken to be

\[ u(\ell) = \frac{9k^3}{\ell} \]  \hspace{1cm} (3a)

or

\[ u(\ell) = \frac{72 k^{1.1}}{\ell} \]  \hspace{1cm} (2b) respectively.

A computer program was written to perform these calculations.

The integrals on the right hand side of equations (1a) and (1b) were evaluated using a Simpson's rule integration. The bubble diameters measured on the electrode surface were sorted into an odd number of size intervals. The fraction of bubbles in each interval, \( f(\tilde{\ell}) \), was then calculated by dividing the number of bubbles in each interval by the total number of bubbles measured (subroutine "Interval"). The value of the integrand could then be evaluated by multiplying \( f(\tilde{\ell}) \) by \( \tilde{\ell}^{n-2} \) or \( \tilde{\ell}^{n-3} \) depending on whether equation (1a) or (1b) is being used, where \( \tilde{\ell} \) is the bubble diameter at the mid point of the respective interval, and
n is the order of the moment being considered (lines 1080 - 1110).

Hence:

\[ \int_{-\infty}^{\infty} p(t) dt = \frac{h}{3} \left[ p_1 + 4p_2 + 2p_3 + 4p_4 + \ldots + 4p_{m-3} + 2p_{m-2} + 4p_{m-1} + p_m \right] \]

Where \( p(\cdot) \) is the integrand of equation (1a) or (1b)

- \( h \) = interval length
- \( p_i \) = value of the integrand in the \( i^{th} \) interval
- \( m \) = number of intervals (\( m \) must be an odd number)

Having evaluated the integral (subroutine "Integrate"), \( q_{n} \) can be evaluated from (1a) or (1b) (lines 1130 - 1140) since the constants in front of the integral are known quantities (\( \bar{l} \) is simply the mean of bubble sizes on the surface).

Having evaluated \( q_{n} \), an assumption about the distribution leaving the surface is made. Either a normal or a gamma distribution can be assumed.

The parameters of the required distributions are then evaluated and the moments of this distribution can be calculated (lines 1290 - 1560) as outlined in appendix 2. The results are printed out in subroutine "Output".

The results are presented in section 4. Sample print outs are presented after the program listing. These samples show the output of the program when first a normal and then a gamma distribution is assumed and either equation (2a) or (2b) is used to describe the rate of bubble growth. The results are all for the same run.
n is the order of the moment being considered (lines 1080 - 1110).

Hence:

\[
\int_{0}^{x} p(t) \, dt = \frac{h}{3} \left( p_1 + 4p_2 + 1p_3 + 4p_4 + \ldots + 4p_{m-3} + 2p_{m-2} + 4p_{m-1} + p_m \right)
\]

Where \( p(t) \) is the integrand of equation (1a) or (1b):

- \( h \) = interval length
- \( p_i \) = value of the integrand in the \( i^{th} \) interval
- \( m \) = number of intervals (\( m \) must be an odd number)

Having evaluated the integral (subroutine "Integrate"), \( q_{n} \) can be evaluated from (1a) or (1b) (lines 1130 - 1140) since the constants in front of the integral are known quantities (\( \bar{Z} \) is simply the mean of bubble sizes on the surface).

Having evaluated \( q_{n} \), an assumption about the distribution leaving the surface is made. Either a normal or a gamma distribution can be assumed. The parameters of the required distributions are then evaluated and the moments of this distribution can be calculated (lines 1290 - 1560) as outlined in appendix 2. The results are printed out in subroutine "Output". The results are presented in section 4. Sample print outs are presented after the program listing. These samples show the output of the program when first a normal and then a gamma distribution is assumed and either equation (2a) or (2b) is used to describe the rate of bubble growth. The results are all for the same run.
A program to calculate the moments of the distributions of the
bubbles on and leaving the electrode surface.

The parameters k, a, and W in the population balance are also
calculated. Allowance is made for the assumption of a normal
distribution of bubbles leaving the electrode surface. The necessary changes in the program to allow for
these assumptions are shown in lines 1410-1600, 3620-3660.

OPTION PAGE 1

CONTROL 1,121

GRAPHICS OFF

OUTPUT 2 USING 'X,K,PK' CLEAR the screen

GOSUS READ 1 Read in the bubble diameters on the surface

DO

PI=3 Defines plotter position

PRINT X Print X

$ "INTERVAL," Defines printer position

PLOTTER IS Print P

PLOTTER IS Print P

GO TO SUBROUTINE

Calculate the mean bubble diameter on the electrode surface

\[ \text{Mean} = \frac{\sum \text{Data}}{N} \]

Calculate the standard deviation of the bubble diameters

\[ \text{Stddev} = \sqrt{\frac{1}{N-1} \left( \sum (\text{Data} - \text{Mean})^2 \right)} \]

PRINT USING 328,Mean,Stddev

Image "The mean bubble is \( \text{Mean} \) microns, " Standard deviation is \( \text{Stddev} \) microns"

Smallest=MIN(Data) Largest=MAX(Data)

Smallest=Smallest Smallest=Smallest Smallest=Smallest Smallest=Smallest

Largest=MAX(Data) Largest=MAX(Data) Largest=MAX(Data)

PRINT USING 328,Largest,Smallest

Image "The largest bubble is \( \text{Largest} \) microns, " The smallest bubble is \( \text{Smallest} \) microns"

GO TO SUBROUTINE "Interval" To sort the bubble diameters into intervals

INTERVAL CALL INTERVAL(M,Data(1),Interval(1),Divide,Divlen,Largest,Smallest)

GO TO SUBROUTINE "Print" To display the intervals on the screen

PRINT CALL INTERVAL(M,Data(1),Interval(1),Divide,Divlen,Largest,Smallest)

IF Printr=78 THEN Print CALL since the no. of intervals has been decided

INPUT "Do you wish to change the number of intervals?", N

IF UP(X+541,11,11)=Y THEN

GOTO INTERVAL_CALL and \text{Div} \text{len} \text{int} into new no. of intervals

ELSE

INPUT "Do you want to print the results?", N

IF UP(N+411,13)=Y THEN

Printr=781

GOTO Print CALL and print result to the external printer.
520 END IF
530 END IF

540 ! SUBROUTINE 'Plp' draws a histogram of the bubble diameters measured
550 ! on the electrode surface. This is the same routine as subroutine
560 ! 'PI' in Appendix 2.

570 Plot_call: CALL Plot(Plr,Plr,Fil,Draw,Drawen,Line,Lineen,Largest,Smallest,Mean,Stddev,Interval:W)
580 OUTPUT 2 USING","",""CLEAR SCREEN
590 IF Plr<75 THEN Plr=75
600 Ys="**
610 INPUT "Do you wish to make any changes?", J
620 IF UPCase(Ys(J))="Y" THEN
630 GOTO Interval_call 1 to change the number of intervals
640 ELSE
650 Ys="**
660 INPUT "Do you want a hard copy?", R
670 IF UPCase(Ys(J))="Y" THEN
680 Plr=75
690 Ps="HPGL"
700 GOTO Plot_call 1 to plot the histogram on the plotter
710 END IF
720 END IF
520 END IF
530 END IF!
540 SUBROUTINE 'Plot' draws a histogram of the bubble diameters measured
550 on the electrode surface. This is the same routine as subroutine
560 'Plot' in Appendix 2.
570 Plot call: CALL Plot(Pltr,Pt,File#,Div=,Divlen,Largest,Smallest,Mean,Stdev,Interval(#),H)
580 OUTPUT 2 USING ";*","*" ; CLEAR SCREEN
590 IF Pltr=705 THEN Plot programs
600 Ys="**
610 INPUT "Do you wish to make any changes?",Ys
620 IF UPCH$(Ys(1))="Y" THEN
630 GOTO Interval call 1 to change the number of intervals.
640 ELSE
650 Ns="**
660 INPUT "Do you want a hard copy?",Ns
670 IF UPCH$(Ns(1))="Y" THEN
680 Pltr=705
690 P#="MPGL'
700 GOTO Plot call 1 to plot the histogram on the plotter.
710 END IF
720 END IF!
730 Fit_pro: ' Start of the moments calculation.

740 CONTROL 1,12:4
750 Prntent ! This variable defines the printer location as the screen.
760 GRAPHICS OFF
770 OUTPUT 2 USING "#X";"WX" ! Clears alpha screen.
780 Rate_flag=0 ! This variable will define which rate equation is used.
790 FOR I=1 TO 7
800 DM KEY 1 GOSUB Dummy ! This loop will
810 NEXT I
811 ! switch off the soft keys
812 NEXT I
815 ! that are not needed.

820 DM KEY 8 LABEL "U=xt^1/2" GOSUB U_half ! This key selects the rate
821 ! Equation U=xt^1/2
830 DM KEY 9 LABEL "U=xt^2/3" GOSUB U_thirds ! This key selects the rate
831 ! Equation U=xt^2/3

840 PRINTER IS Prnter
850 PRINT "Use soft keys to select a rate equation"
860 DM CYCLE .3 GOTO Check ! and see if a rate equation has been selected.
870 Haver:GOTO Haver ! until a rate equation has been chosen.

880 Carry_en:DM KEY 8 GOSUB Dummy ! This deactivates the
890 DM KEY 9 GOSUB Dummy ! soft keys after a rate
900 CONTROL 1,12:1 ! equation has been selected
910 OUTPUT 2 USING "#X","WX" ! Clear alpha screen
920 No_int=Divma ! Number of intervals

930 ALLOCATE F(1:No_int),L(1:No_int) ! Check to see
940 IF Rate_flag=2 THEN ! which rate
950 Const=(#2533#3383#313383#633.5)/19684.6133.6 ! const is
960 END IF ! used & then
970 IF Rate_flag=3 THEN ! evaluate the
980 Const=(#2533#3383#313383#5)/19684.6 ! constant in
990 END IF ! front of the
1000 ! integral.
1010 IF Rate_flag=2 AND Rate_flag=3 THEN ! Make sure
1020 BEEP 158 ! Rate_flag
1030 DISP "OPPS !!!!!!!!!!!!!!!!!!!!!" ! has not
1040 STOP ! obtained
1050 END IF ! another
1060 ! value.
1070 !
1080 FOR I=1 TO No_int ! Loop to find I
1090 L(I)=Smallest+100*Divlen-Divlen/2*E-6 ! at the experimental
1100 NEXT I ! points.

1110 OUTPUT 2 USING "#X","WX" ! Clear the screen
1120 !
1130 ! THIS LOOP CALCULATES THE MOMENTS
1140 ! No_of_moms=10 ! the number of moments to be calculated.
1150 ALLOCATE v,bet(1:No_of_moms),bet(1:No_of_moms),wit(1:No_of_moms)
1160 OUTPUT 2 USING "#X","WX" ! Clear the screen
1170 FOR I=1 TO No_of_moms ! Allocate function evaluations to evaluate the moments of g(I).
1180 ALLOCATE Func(1:No_eval)
1199 !
1200 FOR I=1 TO No_of_moms!
For I = 1 TO #a_int
    If Rate_flag = 2 THEN F(J)=V*#aInterval(J)*(J-1)/2
    If Rate_flag = 1 THEN F(J)=V*#aInterval(J)*(J-1)/4
Next J

Call Integrate(F(J),#a_int,Dividens,#b_int,Integral)

Integrate=Integral/Const*10

For I = 1 TO #a_int
    H=H*#Sigma/#a_eval
        Next I

Call Integrate(F(J),#a_int,Integral)

Evaluate the integrals.

For I = 1 TO #a_of_moments
    FOR J = 1 TO #a_eval
        Step_len(Next_length)=#Sigma*(#a_eval-1)/2
        Func(J)=Step_len^#aExp(-(Step_len-H))/#Sigma/#aEval/(#Sigma^2+2*#Sigma)
    Next I
    Call Integrate(Func(J),#a_eval,H,Integral)
        to evaluate the moments.
    Beta(J)=Integral/const
        to calculate the moments.
    Q(J)=Q Beta(J)/Beta(J) = q calculated from betas.
Next J

Call 1570

If a gamma distribution is required lines 1291 to 1421 should be replaced by the following program lines:

Call Gam.a((N_a_eval/#a_mean)^2)*(N_a_eval/#a_mean)^2)

Call Gam.b((N_a_eval/#a_mean)^2)*(N_a_eval/#a_mean)^2)

For I = 1 TO #a_of_moments
    Beta(N)=Beta(N)/(Gam.a*I)

Next I

FOR I = 1 TO #a_b
    Beta(N)=Beta(N)/(Gam.a*N)
        to calculate the moments.
    Q(N)=Q Beta(N)/Beta(N)
        to calculate q from beta's.
Next N

Now print the results using subroutine 'Output'.

If a gamma distribution was assumed then replace the parameters

'Mean' AND 'Sigma' in line 1582 with 'Gam.a' AND 'Gam.b'.

Call Distor(File,Viscosity,Current,Flow,Rate_flag,Winp:Hero,Sigma,\Beta,(N_a_eval,#a_of_moments,#b,Mean,#a Eval,#a_stdev,#a_stdev,#a_calc,\en)

Input "Do you want to change the number of intervals?", Y

Call Locate(F(J),L(J),#a_calc(#a,Beta(J),Func(J),#a)

If Input("0",1,1)="Y" THEN Internal call to change the number of intervals

Y**" 

Input "Do you want to change the rate expression?", Y

Call Locate(F(J),L(J),#a_calc(#a,Beta(J),Func(J),#a)

If Input("0",1,1)="Y" THEN Fit_flag 1 to change the rate equation used.

Control 1,12,0  Switch off keys.

Print Test IS 1

Stop
1210  FOR J=1 TO N_e_int  ! Loop to
1220  IF Rate_flag2 THEN F(J)=E+&Interval(J)*!(J-1-2)  ! evaluate the
1230  IF Rate_flag3 THEN F(J)=E+&Interval(J)*!(J-1-3)  ! integrand
1240  NEXT J  ! at each J.
1250  CALL Integrate(F,K,K_e_int,Divlen,E-6,Integr3) ! Evaluate the integral
1260  Integr3=Integr3+Integr3*Const3!  
1270  Q.beta(I)=Integr3+q(beta(I))  
1280  NEXT I  
1290  Q.Eval=Mean(E-6)  ! Mean
1300  Sigma=Stddev(E-6)  ! Standard deviation
1310  H=Sigma/(No_eal+1)  ! Step length for integrating q(I).
1320  EVALUATE THE INTEGRAL 1-#q(I) i THE n th M0MENT.
1330  FOR J=1 TO N_e_moments
1340  FOR I=J TO N_e_eal
1350  Step_len=Step_len+((Q.beta(I)+Q.beta(J))/2)  
1360  Func(I+J)=Step_len**2  
1370  NEXT I  
1380  CALL Integrate(Func(I),No_eal,H,Integr3)  
1390  NEXT I  
1400  Beta(I)=Integr3+q(beta(I))  ! q calculated from beta(I).
1410  NEXT I  !
1420  GOTO 1570
1430  !+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
1440  IF a gamma distribution is required lines 1291 to 1421 could be
1450  replaced by the following program lines:
1460  Gam.a=((Q.beta(I)+Q.beta(J))/2)-1)  ! Evaluate a & b parameters in
1470  Gam.b=Q.beta(I)/Q.beta(J)  ! gamma distribution.
1480  FOR J=1 TO N_e_moments
1490  Beta(I)=Beta(I)*Gam.a+Gam.b  
1500  NEXT I  
1510  FOR I=1 TO N
1520  Beta(I)=Beta(I)*Gam.a  
1530  NEXT I  
1540  Gam.a=Gam.a/Gam.b  
1550  NEXT I  
1560  !+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
1570  Q.calc=Q.calc*Calc(100)!(281100000.6423.58Beta(I))  
1580  ! HOW PRINT OUT THE RESULTS USING SUBROUTINE 'Output'.
1590  ! IF A GAMMA DISTRIBUTION WAS ASSUMED THEN REPLACE THE PARAMETERS
1600  ! 'Beta' AND 'Signal' IN LINE 1629 WITH 'Gam.a' AND 'Gam.b'.
1610  CALL Output(File,Viscosity,Current,Flow,Rate_flag,0,1)  
1620  ! 'Beta' AND 'Signal' IN LINE 1629 WITH 'Gam.a' AND 'Gam.b'.
1630  T='*
1640  INPUT "Do you want to change the number of intervals?",Y
1650  DEALLOCATE(F,K,K_e_int,Divlen,E-6,Beta(I),Func(I),Q)
1660  IF UPC(111,111)="Y" THEN Interval_call ! to change the n. of intervals
1670  T='*
1680  INPUT "Do you want to change the rate expression?",Y
1690  IF UPC(111,111)="Y" THEN Fit_flag ! to change the rate equation used.
1700  CONTROL 1,12,0  ! Switch aff keys.
1710  PRINTER IS 1  
1720  STOP 1
1736 Dummy: RETURN  | Dummy routine to deactivate the soft keys.

1740 U_half: Rate_Flag=2  | Defines the rate equation
1750 RETURN                | as \( U = t^{-1/2} \).

1760 U_2_thirds: Rate_Flag=3 | Defines the rate equation
1770 RETURN                 | as \( U = t^{-2/3} \)

1780 Read: | Read data off the disc.
1790 MASS STORAGE IS "MP121,780."
1600 INPUT "Enter the name of the data file",File$;
1610 ASSIGN File TO File$;
1620 ENTER File,File,M,Viscosity,Current,Flow; | Reads in the viscosity, current and flow rate used.
1630 ALLOCATE Data(M),Dummy(M),Interval(M);
1650 ENTER File,2,Data(0);
1660 ASSIGN File TO %;
1670 INPUT "Enter the mean and standard deviation of bubble diameters leaving the surface",Movie_mean,Movie_stdev;
1680 INPUT "Enter the value of \( N \)\(^{\text{th}}\) on \( N \) of nucleation sites per unit area"
1690 RETURN 1

1900 Check: IF Rate_Flag=2 OR Rate_Flag=3 THEN | Checks to see if a rate equation
1910 OFF CYCLE                 | has been chosen.
1920 GOTO Carry_on             | If so continue with calculations
1930 ELSE                      | otherwise wait
1940 GOTO Hover                 | until one is entered
1950 END IF
1960 END 1
1974 Integrate:SUB Integrate(F(i),N0,int,H,Integral) ! Using Simpson's Rule.
1980 Integral=Integral+F(i)*F(N0,int)
1990 FOR I=2 TO N0,int-1 STEP 2
2000 Integral=Integral+4*F(I)
2010 NEXT I
2020 FOR I=3 TO N0,int-2 STEP 2
2030 Integral=Integral+2*F(I)
2040 NEXT I
2050 Integral=Integral*h/3
2060 SURENO !
2070 ! Using Simpson's Rule.
2080 ! Start adding.
2090 ! Add the 48 terms.
2100 ! Add the 28 terms.
2110 ! Multiply by h/3.
2070 INTERVAL: SUB INTERVAL(M,Data1),Interval(1),Div1n,Divlen,Largest,Smallest
2080 OPTION BASE 1
2090 INPUT "Enter the number of intervals you require - make sure its an odd number",Div
2100 IF Div=1 OR FRACT(Div/1)=0 OR FRACT(Div/2)=1 THEN
2110 G"TOP 500,1
2120 DISP "THAT IS NOT FUNNY"
2130 WAIT 2
2140 GOTO 299
2150 END IF
2160 REDIM Interval(Divn) Interval1=number of bubbles in each interval
2170 MAT Interval1(*)
2180 Divlen=Largest/Smallest)/Divlen Divlen=length of each interval
2190 ! Loop to place each bubble in its correct interval
2200 FOR I=1 TO N
2210 FOR J=1 TO Divn
2220 IF Data(I)=Smallest/Divlen AND Data(I)=Smallest+(J-1)Divlen THEN
2230 Interval(J)=Interval(J)+1
2240 GOTO Skip
2250 END IF
2260 NEXT J
2270 BEEP 508,1
2280 DISP "ERROR IN 1811"
2290 STOP
2300 Skip:NEXT I
2310 MAT Interval(1/N)*Interval
2320 SUBEND
2330 Print:SUB Print(Viscosity,Current,Flow,Prnr,N,Largest,Smallest,Div1n,Divlen,Mean,Stddev,Interval(1))
2340 PRINTER IS Prnt
2350 IF Prnt THEN PRINT CHR$(12) + CLEARSCREEN
2360 PRINT USING 2370;Viscosity,Current,Flow
2370 IMAGE "Solution viscosity is ";#," centipoise","Current used was ";#," microliters/","The flow rate is ";#," 1/min","/;
2380 PRINT "The number of points used is ";N
2390 PRINT USING 2400;Mean,Stddev
2400 IMAGE "Mean bubble diameter = ";.,".000,000," microns","Standard deviation = ";.,".000,000," microns"
2410 PRINT USING 2420;Largest,Smallest
2420 IMAGE "Largest bubble diameter = ";.,".000,000," microns","Smallest bubble diameter = ";.,".000,000," microns","/;
2430 PRINT 1"INTERVAL NUMBER",TAB(21),"INTERVAL RANGE (microns",TAB(40),"FRACTION OF BUBBLES"
2440 PRINT "-------------------------",TAB(21),"-------------------------",TAB(40),"-------------------------"
2450 FOR I=1 TO Divn
2460 Y(I,1)=INT(Y(I,1)(Smallest+(I-1)*Divlen)*100)/100
2470 Y(I,2)=INT(Y(I,2)(Smallest+(I-1)*Divlen)*100)/100
2480 PRINT USING 2500;Y(I,1),Y(I,2),Interval(I)
2490 IMAGE S1,.00,.000,000,K,251,D,0000
2510 NEXT I
2520 SUBEND !
SUB Plat(Plt, P#, File#, Dialen, Diverse, Largest, Smallest, Mean,Stddev, Interval(I), N)

OPTION BASE 1

Plt: Ploting routine

Top=MAX(interval(I))  ' Top = SIZE OF LARGEST INTERVAL
Top=INT(Top&10)*1/10
PLOTTER IS Plt,P#
ALPHA OFF

IF Plt+3 THEN CLEAR
IF Plt+3 THEN 2700! 1f the plotter isn't the screen then pick up a pen
GRAPHICS OFF

OUTPUT 2 USING 'X'; 'VI'

DISP 'Put a pen in the plotter and press 'DRAW' when ready'
PAUSE
ALPHA OFF
GRAPHICS ON

OUTPUT 705; 'SPI'!* Pick up a pen

LINE TYPE .
LDIR 0
WINDOW Smallest-2*Dialen,Largest+Dialen/2,-Top/5 Top/3 Plt scale
LONG 5
CSIZE 1.5
CLIP Smallest,Largest,0,Top
AXES Dialen,.5,Smallest,.! draw axes
CLIP OFF !

! Draw histogram

FOR I=1 TO Diani
IF Interval(I)=0 THEN 2840
CLIP Smallest+I*Dialen,Smallest+I*Dialen,S,Interval(I)
FRAME
NEXT I
CLIP OFF
CSIZE 3,5
LONG 5!

! Label X axis

FOR I=1 TO Diani
MOVE Smallest+I*Dialen,-Top/30
LABEL USING "000.00"; Smallest+I*Dialen
NEXT I
MOVE Largest+Smallest*.7,-Top/10
CSIZE 5,.5
LABEL "Bubble diameter (microns)"
CSIZE 3,.5!

! Label Y axis

FOR I=1 TO Top STEP .15
MOVE Smallest-Dialen/4,.1
LABEL USING "2.000.00"; I
NEXT I
CSIZE 4,.5
MOVE Smallest-Dialen,Top/2
LDIR 90
LONG 6
LABEL "Fractions of bubbles!

! Graph heading
MOVE Mean,0
IDRAW 1,Top
MOVE -Stddev,1
LINE TYPE 1
SIZE 2,5
LABEL CH4(124)
MOVE Mean-Stddev,Top
IDRAW 2R(Stddev,0
LABEL CH4(124)
MOVE Mean,Top
LDAG 4
LABEL "x"
MOVE Mean+Stddev/2,Top
LABEL "+S"
MOVE Mean+Stddev/2,Top
LABEL "-S"
MOVE Smallest,0
FOR I=Smallest TO Largest STEP Divlen/11
Exponent=Divlen*EXP(-(I-Mean)^2/2)/Stddev*SIGM(2PI)
DIV 1,Exponent
NEXT I
IF P1r=3 THEN 3440
OUTPUT 785,"SP" Put pen down
GRAPHICS OFF
SUEEND
DIM A, B
3460 Output SUB Output(File),Viscosity,Current,Flow,Rate_Flag,Out,H,eta,Sigma,0,Beta(1),No_of_moments,Beta(2),devise_minus
3470 Print "Meas,Stddev,Mean,Stddev,0,calc",Men
3480 PI 701; WIDTH (80) Output to printer
3490 Print "4665",":File)="466A"
3500 Print N
3510 Print USING "$20.000","Meas,Stddev,Mean,Stddev,0,calc","Viscosity,Current,Flow
3520 Print USING "30.000","Viscosity,Current,Flow"
3530 Print USING "20.000","Current,Viscosity,Flow"
3540 Print USING "20.000","Flow,Viscosity,Current"
3550 Print USING "20.000","Viscosity,Current,Flow"
3560 Print USING "20.000","Current,Viscosity,Flow"
3570 Print USING "20.000","Viscosity,Current,Flow"
3580 Print USING "20.000","Current,Viscosity,Flow"
3590 Print USING "20.000","Viscosity,Current,Flow"
3600 Print USING "20.000","Current,Viscosity,Flow"
3610 If a normal distribution was assumed then change line 360 accordingly
3620 If a gamma distribution was assumed then change line 360 accordingly
3630 Input USING 3640;H,eta,Sigma,Beta(1)
3640 Input USING 3640;H,eta,Sigma,Beta(1)
3650 If a gamma distribution was assumed then line 3640 should read
3660 Input USING 3640;H,eta,Sigma,Beta(1)
3670 Print USING 3680
3680 Print USING "3680","H,eta,Sigma,Beta(1)
3690 Print USING 3690;Q,calc
3700 Print USING 3690;Q,calc
3710 PRINT USING 3690;Q,calc
3720 PRINT USING 3690;Q,calc
3730 PRINT USING 3690;Q,calc
3740 PRINT USING 3700;H,eta,Sigma
3750 PRINT USING 3700;H,eta,Sigma
3760 PRINT USING 3700;H,eta,Sigma
3770 Print USING 3710;H,eta,Sigma,Beta(1)
3780 Print USING 3710;H,eta,Sigma,Beta(1)
3790 Print USING 3710;H,eta,Sigma,Beta(1)
3800 Print USING 3720;H,eta,Sigma,Beta(1)
3810 Print USING 3720;H,eta,Sigma,Beta(1)
3820 Print USING 3720;H,eta,Sigma,Beta(1)
3830 Print USING 3730;H,eta,Sigma,Beta(1)
3840 END IF
3850 IF Rate_Flag2 THEN 
3860 Print "1121"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"
3870 PRINT USING 3740
3880 Print USING 3750
3890 Print USING 3760
3900 Print USING 3770;H,eta,Sigma,Beta(1)
3910 Print USING 3770;H,eta,Sigma,Beta(1)
3920 Print USING 3770;H,eta,Sigma,Beta(1)
3930 END IF
3940 IF Rate_Flag=0 THEN 
3950 PRINT USING 3780;H,eta,Sigma,Beta(1)
3960 Print USING 3790;H,eta,Sigma,Beta(1)
3970 Print USING 3800;H,eta,Sigma,Beta(1)
3980 Print USING 3810;H,eta,Sigma,Beta(1)
3990 Print USING 3820;H,eta,Sigma,Beta(1)
4000 NEXT IF
4010 PRINT "4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"=4112"
4020 PRINT USING 3830
4030 $
Solution mass flow rate: 1.0E-3
Total current: 0.1 A
Flow rate: 0.6 L/min

<table>
<thead>
<tr>
<th>Average bubble diameter on the surface</th>
<th>Standard deviation of bubble diameters on the surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.740 microns</td>
<td>21.705 microns</td>
</tr>
</tbody>
</table>

Assuming a normal distribution of bubble diameters leaving the surface:

\[ N = \frac{27000E-04 \text{ m}}{6000E-05 \text{ m}} \]  
(calculated from the 3rd moment)

<table>
<thead>
<tr>
<th>Mass flow rate m³/min</th>
<th>B (predicted)</th>
<th>( u ) (1/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1500E+02</td>
<td>1.26548E-1</td>
<td>3.9563E+06</td>
</tr>
<tr>
<td>0.5250E+02</td>
<td>1.73196E-03</td>
<td>4.0143E+06</td>
</tr>
<tr>
<td>2.0179E-05</td>
<td>2.51636E-12</td>
<td>4.0287E+06</td>
</tr>
<tr>
<td>0.26399E-06</td>
<td>2.84392E-16</td>
<td>3.9889E+06</td>
</tr>
<tr>
<td>5.3165E-13</td>
<td>3.12532E-20</td>
<td>3.5332E+06</td>
</tr>
<tr>
<td>1.9127E-17</td>
<td>1.01304E-23</td>
<td>1.8875E+06</td>
</tr>
<tr>
<td>2.38658E-21</td>
<td>1.73061E-27</td>
<td>1.3790E+06</td>
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<tr>
<td>3.8326E-29</td>
<td>6.4214E-31</td>
<td>9.9540E+05</td>
</tr>
<tr>
<td>1.0122E-31</td>
<td>4.8495E-35</td>
<td>1.1332E+05</td>
</tr>
<tr>
<td>1.73061E-37</td>
<td>0.01122E-3</td>
<td>5.0986E+05</td>
</tr>
</tbody>
</table>
Solution viscosity = 0.92 cP
Total current = 1 A
Flowrate = 2.1 m/s

Average bubble diameter on the surface
Standard deviation of bubble diameters on the surface

Average bubble diameter on the surface
Standard deviation of bubble diameters on

Assuming a normal distribution of bubble diameter leaving the surface

Net a = 1.270000E-04 m
Sigma = 3.600000E-05 m

\[ q = 3.87445E+06 \text{ m}^{-2} \text{s}^{-1} \quad \text{(calculated from the 3rd moment of)} \]

\[ N = 8.966E+06 \text{ m}^{-2} \]

\[ \eta(1) = 144(k^3)/(1.2) \]

where \( k = 4.49E-05 \text{ m/s}^{1/3} \)

<table>
<thead>
<tr>
<th>i</th>
<th>( q\cdot B_i \text{(calc)} \text{ (m}^3/\text{m}^2\text{s}) )</th>
<th>( B_i \text{(predicted)} \text{ m} )</th>
<th>( 2.811 \text{ m/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.115E+02</td>
<td>1.26548E-04</td>
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<tr>
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<td>4.03231E+06</td>
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<tr>
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<td>3.84322E-16</td>
<td>3.21210E+06</td>
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<td>2.8899E+06</td>
</tr>
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<td>1.01304E-23</td>
<td>2.63105E+06</td>
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<td>1.97977E-21</td>
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<td>8</td>
<td>2.42041E-25</td>
<td>3.04214E-31</td>
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<tr>
<td>9</td>
<td>3.02308E-29</td>
<td>5.48455E-35</td>
<td>5.51199E+05</td>
</tr>
<tr>
<td>10</td>
<td>3.85749E-33</td>
<td>1.01122E-38</td>
<td>3.81488E+05</td>
</tr>
</tbody>
</table>
Solution viscosity = 0.92 CP  
Total current = 1 A  
Flowrate = 2 l/min

Average bubble diameter on the surface  
Standard deviation of bubble diameters on the surface  
= 88.740 microns  
= 21.705 microns

Average bubble diameter on the surface  
Standard deviation of bubble diameters on the surface  
= 127.000 microns  
= 36.000 microns

Assuming a gamma distribution of bubble diameters leaving the surface:

\[ a = 1.14452E+01 \]
\[ b = 9.79938E+04 \text{ l/m} \]

\[ q = 3.79563E+06 \text{ m}^{-2} \text{s}^{-1} \] (calculated from the 3rd moment)

\[ N = 8.966E+06 \text{ m}^{-2} \]

\[ u(1) = 8(k^2) / l \]

where \( k = 3.20E-05 \text{ m/s}^{1/2} \)

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<tr>
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<th>( \eta B_i(\text{calc}) \text{ (m}^4/\text{m}^2\text{s}) )</th>
<th>( B_i(\text{predicted}) \text{ (m}^4)</th>
<th>( q_i(1/\text{m}^2\text{s}) )</th>
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<td>4.55029E+02</td>
<td>1.2700E-04</td>
<td>3.58283E+06</td>
</tr>
<tr>
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<td>1.74259E-08</td>
<td>4.37455E+06</td>
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<tr>
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<td>2.06270E-38</td>
<td>2.49574E+05</td>
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Solution viscosity = 0.92 cP
Total current = 1 A
Flowrate = 2 l/min

Average bubble diameter on the surface = 88.740 microns
Standard deviation of bubble diameters on the surface = 21.705 microns

Average bubble diameter on the surface = 127.000 microns
Standard deviation of bubble diameters on the surface = 36.000 microns

Assuming a gamma distribution of bubble diameters leaving the surface:

\[ a = 1.1445 \times 10^4 \text{ m}^{-1} \]
\[ b = 9.79938 \times 10^4 \text{ m}^{-1} \]
\[ q = 3.79563 \times 10^6 \text{ m}^{-2} \text{s}^{-1} \]

\[ N = 8.966 \times 10^6 \text{ m}^{-2} \]

\[ u(1) = \frac{B(k^2)}{1} \]
where \( k = 3.20 \times 10^{-5} \text{ m/s}^{1/2} \)

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Solution viscosity = 0.92 cP
Total current = 1 A
Flowrate = 2 l/min

Average bubble diameter on the surface
Standard deviation of bubble diameters on the surface = 88.740 microns

Average bubble diameter on the surface
Standard deviation of bubble diameters on the surface = 21.705 microns

Average bubble diameter on the surface
Standard deviation of bubble diameters on the surface = 127.000 microns

Average bubble diameter on the surface
Standard deviation of bubble diameters on the surface = 36.000 microns

Assuming a gamma distribution of bubble diameters leaving the surface:

\[ a = 1.14452E+01 \]
\[ b = 9.79938E+04 \quad \text{1/m} \]

\[ q = 3.79563E+06 \quad \text{m}^{-2} \times \text{1} \quad (\text{calculated from the 3rd moment}) \]

\[ N = 8.966E+06 \quad \text{m}^{-2} \]

\[ u(1) = 144(k^3)/(1^2) \]

where \( k = 4.49E-05 \quad \text{m/s}^{1/3} \)

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Author  Hoffman D L
Name of thesis  Application of population balance models to the study of nucleation and growth of bubbles produced at gas evolving electrodes  1984

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