Chemical Acoustic Emission Analysis of the Briggs-Rauscher Iodine Clock

by

Ivan Heinz Brock

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ABSTRACT

The oscillations observed in the Briggs-Rauscher Iodine Clock were studied using chemical acoustic emission (CAE) analysis. The experimental system evolved through three separate designs. The first early design employed a batch delivery system and utilized a piezoelectric transducer as the CAE sensor. The second design employed a flow delivery system and the oscillating reaction was monitored simultaneously by CAE, ultraviolet-visible spectrophotometry, and an ion-selective electrode. Sampling periods of 4.0 seconds made this a "low resolution" system. The third design was an optimized version of the second, with shorter sampling periods (1.0 seconds), which led to higher resolution data.

The concentrations of the reagents used in the first system were those recommended by Briggs and Rauscher. Four unique phases of the oscillator were observed. The peak slopes during the positive slope phase increased according to second order kinetics, and the decreasing peak slopes during the negative slope phase were found to be independent of reagent concentration. Analysis of the averaged power spectra revealed two distinct frequency regions. Chemometric analysis successfully identified signals due to noise.

A series of experiments were conducted in which [iodate] varied over a range of \textit{ca.} 0.004 to 0.037 M at three different temperatures: 25, 30 and 35°C. It was discovered that the number of oscillations (both CAE and iodine oscillations) was independent of temperature. The CAE peak rates (increase and decrease) were also found to be independent of temperature while the iodine production and consumption rates were found to \textit{ca.} triple with each five degree rise in temperature. Integrated CAE d.c. rates followed second order kinetics.

Another series of experiments were conducted in which \textsubscript{2}O\textsubscript{2} was varied over the range of \textit{ca.} 0.078 to 0.78 M at 35°C. The number of observed CAE oscillations was found
to be independent of initial \([\text{H}_2\text{O}_2]\) while the number of iodine oscillations increased as initial \([\text{H}_2\text{O}_2]\) increased. Integrated CAE d.c. rates followed no simple trend.

Under the conditions examined, a minimum [iodate] of 0.019 M, and \([\text{H}_2\text{O}_2]\) of 0.16 M was required for oscillations to commence. Periodicity in the CAE data was noted in those experiments which did not strongly oscillate and attributed to a dissolved oxygen model.

A refinement of the currently accepted mechanism is proposed and the utility of CAE as a tool to investigate oscillatory kinetics is discussed.
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GLOSSARY

a.c. (alternating current).

a/d analog to digital convertor. see DACA.

CAE (chemical acoustic emission).

CV % coefficients of variance, expressed as a percentage. This parameter is used to
gauge the accuracy of a fitted curve. It is computed as the normalized
version of the standard error:

CV % = 100% * std.err. in parameter value

d/a digital to analog convertor. see DACA.

DACA (data acquisition and control adapter). The primary interface used in this
work. It has a max. 15 kHz sampling rate, 4 (12-bit) a/d devices, 2 (12-bit)
d/a devices and 16 binary (TTL) i/o lines.

dB (decibel). The logarithm of the ratio of the output signal to the input signal,
multiplied by 20. Mathematically, dB = 20 log (I/I_o).

digitize render a continuous signal into a set of [evenly spaced] discrete data points.

FIDO (flow injection development and optimization). A flow injection analysis
system developed mostly in-house.

GPIB (general purpose interface bus). A standard for transmitting data and control
commands between electronic equipment. Based on the IEEE-488
specification.

HPIB (Hewlett-Packard interface bus). HP’s version of the GPIB (above).

IEEE-488 see GPIB.

i/o (input/output).

null-modem a standard serial cable with two sets of control lines crossed:
transmit data (TD) to receive data (RD)
request-to-send (RTS) to clear-to-send (CTS)
real-time refers to the processing of data as it is acquired, as opposed to storing the data for processing at a later time.

RS-232 (serial port interface). The standard asynchronous communications adapter found on most personal computers. In this work, the RS-232 was used in conjunction with a null-modem cable to allow two computers to exchange information.

signal has many meanings, depending on context. In this work, "acoustic emission signal" often refers to a collection of 1024 digitized points sampled from a continuous data stream.
Chapter One - Introduction

“What do mean, you’ve got a little job for me?”
- Hercules

This work was started with two goals. The first was to use chemical acoustic emission to investigate the kinetics of a complex chemical reaction. The second was to develop the technology to a level where it could reliably deliver useful chemical information in systems which are perhaps not readily studiable by more conventional analytical methods. These goals are not strictly separate; they are intimately intertwined. The complex chemical reaction studied is the Briggs-Rauscher oscillating iodine clock.

1.1 Acoustic Emission

Acoustic emission is not a new phenomenon. It has been used in material science since the early 1930s\(^1\). The American Society for Testing of Materials adopted acoustic emission as a recognized technique in 1972\(^2\). The range of applications continues to increase with acoustic emission being used to stress-test metals\(^3\), composite materials\(^4\) and polymers\(^5\).
An acoustic emission wave is a transient, elastic wave generated by a rapid mass motion of a collection of atoms. Unlike ultrasonics, where external sound waves are applied, acoustic emission waves are generated from within the material under study.

Physical processes which are known to emit acoustic emission waves include bubble formation, crystal fracture, and phase transitions.

1.2 Chemical Acoustic Emission

Unlike photoacoustic spectroscopy, in which regular pressure fluctuations are measured in response to a chopped beam of radiation, chemical acoustic emission is a passive technique. No stimulation of the chemical reaction is required, reducing the possibility of perturbation.

The first published report of chemical acoustic emission was from van Ooijen et al. in 1978 who noticed audible cracking sounds accompanying the synthesis of dichloro(pyrazine)zinc(II). A limited study of the phenomenon discovered that the intensity of the sound was found to be proportional to the concentrations of pyrazine and zinc chloride. The most intense emissions were found to be at 100 kHz, and the origin of the sound was thought to arise from either the rapid polymerization of short chain segments or an abrupt change in metal coordination (further work by Munro, of this research group, later proved van Ooijen’s hypothesis to be incorrect - acoustic emission from the synthesis of dichloro(pyrazine)zinc(II) was found to be from crystal fracture).

Since van Ooijen’s report, a number of researchers have investigated the potential of chemical acoustic emission as a viable analytical tool. In 1981, Betteridge et al. conducted a survey of different chemical reactions and mixing processes to determine the extent of acoustic activity. The research demonstrated that acoustic emission was
generated from chemical systems as diverse as acid-base reactions, ion-exchange reactions and gel formation. The Briggs-Rauscher iodine clock was also found to be highly acoustically emissive which formed the basis for this work.

Sawada et al. took up acoustic emission research in the early 1980s, with a report of reproducible acoustic emission patterns from the gelation of sodium carbonate with calcium chloride to form calcium carbonate. Plots of acoustic emission intensity as a function of time were successfully used to distinguish three different reaction mechanisms: phase separation, precipitation, and gel formation. Encouraged by these results, Sawada investigated the phase transitions of sodium thiosulfate, p-cresol, water, and select liquid crystalline materials, to discover that acoustic emission accompanies the direction of the transition which results in volume contraction.

In 1989, Lubetkin measured bubble nucleation rates by an acoustic method and found that for supersaturated solutions of CO₂ the rate of bubble nucleation was closely correlated with the rate of bubble bursting at the free liquid surface.

1.3 Acoustic Emission Detection and Analysis

As noted above, acoustic emission as applied to chemical reactions is relatively new and still in exploratory stages. This work is no exception. In the chapters that follow, the reader will witness the evolution of experimental design that led to the development of chemical acoustic emission as a useful analytical tool for solution phase reactions. Each successive experimental layout may differ in the instruments employed, yet there is a common thread. The purpose of this present section is to introduce the general principles behind chemical acoustic emission detection and analysis.
1.3.1 CAE Instrumentation

The simplest acoustic emission instrumentation consists of a sensor, amplifier, and an analog recorder. A system of this nature can be used for simple event counting or analog recording of the continuous signal. It demonstrates the technique’s basic advantages: i.e. it is non-invasive, non-destructive, and inexpensive. More elaborate systems add a spectrum analyzer for real-time frequency analysis or a digitizer for capturing a selected segment of the signal stream.

![Figure 1-1. Block diagram of basic experimental hardware.](image)

The system employed in this study is illustrated as a block diagram in Figure 1-1. A detailed description of the instruments involved is presented in the following chapters. Briefly, the sensor, a piezoelectric crystal, is placed in contact with the reaction vessel through a thin layer of acoustic couplant grease. The crystal transduces the acoustic wave into an a.c. signal which is fed directly into an amplifier. The amplifier optionally applies
a bandpass filter to the amplified signal before passing it onto the digitizer. A d.c. representation of the signal (a peak-detect system with 200 ms time constant) is sent to the analog recorder. The controller, typically a personal computer, supervises the digitizer and provides long-term storage and processing of the data. Shielded cable is used for all connections.

1.3.2 CAE Analysis

In order to realize the potential of acoustic emission for chemical analysis, information about the characteristics of the emissions must be extracted. This information is especially valuable when different mechanisms occur simultaneously\textsuperscript{15}.

Theoretically, there is a large amount of information present within individual signals. However, a signal is a complex transformation of the original emission due to many transmission factors. Despite these distortions, emissions from the same source will often show similar features\textsuperscript{16}. The variability in the emissions results in the characteristics (or features) being described by a population distribution of values rather than a single unique value. Since hundreds or even thousands of emissions may be collected during a single experiment, powerful data reduction and analysis tools are required in order to uncover meaningful information. Unfortunately, commercially available tools of this nature were not suitable for acoustic emission research. Specifically, most data acquisition software was unable to acquire and store emission signals at an adequate rate, and data analysis software lacked the combined spectral analysis and pattern recognition tools required for analyzing chemical acoustic emission data. To overcome this deficiency, a data analysis protocol was established in the laboratory and software written in-house to exploit it.
1.3.2.1 Data Analysis Protocol

The data analysis protocol, or road map, is illustrated in Figure 1-2. Signal acquisition is the obvious first stage, and programs have been written to acquire data from a variety of digitizers. See Appendix B for a complete list of the software written in this laboratory. The acquisition cycle consists of arm/trigger/re-arm sequence in which the digitizer captures a CAE signal when a preset trigger level is breached. This cycle and its limitations are discussed in detail in the experimental sections of the following chapters.

The second stage is signal validation. The purpose of this stage is to ensure that only valid CAE signals are captured and stored. Invalid signals include those which are over-ranged or under-triggered or those due to electrical spikes. An over-ranged signal arises when any part of the acoustic waveform exceeds the dynamic range of the digitizer. An under-triggered signal occurs when the digitizer captures a signal whose trigger level is actually below the requested level. This may be due to trigger level instability or instrument drift. Signals due to electrical spikes are detected through the use of the root mean square (RMS) voltage of the signal. The RMS of each signal is compared to the RMS of known background signals and the signal is flagged for deletion if its RMS value is comparable. This method suffers for experiments which have low signal to noise ratios. In this situation, signal validation based on noise modeling is a better alternative.16
Once signals have been validated, information can be extracted from them using two methodologies. In the first, the raw signal is analyzed directly either by hand or in an automated fashion. Different physicochemical processes commonly produce emissions which have different characteristics in the frequency domain. Though the power spectrum for individual signals from a single experiment can vary appreciably, as discussed earlier, the averaged power spectrum is often highly reproducible. Occasionally more than one acoustically active process will occur during the course of a chemical reaction. In this case, a time-resolved power spectrum may be of greater utility.
In order to produce a time-frequency surface of this nature, some prior knowledge of the temporal behaviour of the chemical system is required.

The acoustic emission of a chemical reaction is monitored as a function of time. Such a series of data measured in time is called a time series. An autocorrelogram is an excellent means of determining the presence of periodicity in a time series data set. To create an autocorrelogram, a new independent variable is created (τ) which represents a time constant. The correlation coefficient, r(τ), can be computed by

\[
    r(\tau) = \frac{\sum_{t=1}^{n-\tau} [(x(t) - \bar{x})(x(t + \tau) - \bar{x})]}{(n - 1 - \tau) \cdot s_x^2}
\]

Eqn. 1-1.

where \( x(t) \) is the value at time \( t \), \( n \) is the number of data points, and \( s_x \) is the standard deviation of \( x(t) \).

The second methodology is based on an indirect analysis of the raw signal. Numerical parameters called descriptors are computed for each signal. A complete list of the 26 descriptors used in this work is presented in Table 1-1. Detailed descriptions of each and their suitability for chemical acoustic emission are published elsewhere. Each signal is then an object which can be represented in a multi-dimensional space consisting of its descriptors as dimensions. Such a data space cannot be visualized and for more than three or four dimensions is inherently difficult to interpret. Fortunately there are a number of chemometric tools which can be employed to assist in the analysis of such highly multivariate data.
1.3.2.2 Multivariate Statistics

Multivariate statistical techniques are necessary for analyzing complicated data such as obtained here. They provide a system for analysis under conditions in which there may be several independent variables and many dependent variables all correlated to varying degrees. Multivariate statistics represent a direct expansion of the more familiar univariate statistics; i.e. multivariate statistics can be seen as the general case, with univariate statistics a simplification of the more general multivariate model. In CAE analysis, descriptive statistics are used to provide a best-guess description of the descriptor populations. When descriptive statistics are used in this way, they are typically called parameter estimates rather than sample statistics.17

Two multivariate statistical tools are used in CAE analysis: rotated principal components analysis (PCA) and non-hierarchical clustering. The most important use of PCA is to represent $n$-dimensional data in a smaller number of dimensions, usually two or three. This is accomplished by projecting a line through the cloud of points in multi-dimensional space such that there is maximum variation along the line and minimum variation around it. Hence the line maintains maximum variation among the data. This is the first principal component. The second component is a line projected orthogonal to the first component, positioned to maximize the variance along its axis. The third component is orthogonal to the first and second, and so on. Each principal component is a new variable made up of a linear combination of the original variables. The coefficients of these variables are the eigenvectors and the variance along the principal component projection is the eigenvalue.

PCA results are likely to be uninterpretable unless rotated. Rotation is only used to improve the interpretability of the solution, it does not change the mathematical fit. The factors may be rotated orthogonally or obliquely. Orthogonal rotation assumes that
the underlying structures producing the results are uncorrelated. Oblique rotation does not make that assumption but the results from an oblique rotation are typically more difficult to interpret.\(^\text{17}\)

In non-hierarchical clustering, one wishes to classify the \(n\)-dimensional descriptor data into \(K\) clusters. The user selects the initial number of clusters, \(K\), and the location of the cluster centers in the \(n\)-dimensional space (or the initial centers are chosen randomly). The algorithm assigns each object (in this case the object is a CAE signal) to one cluster (normally) based on the Euclidean distance between the object and the cluster’s center-of-mass. Once all objects have been assigned, the cluster’s center-of-mass is re-computed and each object is again assigned to the nearest cluster. The cycle is repeated until the same clustering is found in two successive assignment steps.

There are inherent limitations to clustering. The importance of choosing initial cluster centers is magnified if the data contain outliers, thus skewing a cluster’s center-of-mass computation. Then there is the problem of choosing the correct number of clusters with limited or no \textit{a priori} information about the system. Choosing too few clusters will not reveal the structure of the data set and too many clusters may result in a large cluster being subdivided into two smaller ones. Fortunately, there are ways of detecting such problems and compensating for their effects which are discussed more fully in later sections.
Table 1-1 - Descriptors used to characterize individual CAE signals.

<table>
<thead>
<tr>
<th>Descriptor (abbreviation)</th>
<th>Domain</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CREST</td>
<td>Time</td>
<td>ratio of peak voltage to RMS voltage</td>
</tr>
<tr>
<td>KURTOSIS</td>
<td>Time</td>
<td>measure of the deviation from a Gaussian distribution</td>
</tr>
<tr>
<td>T@AREA/2</td>
<td>Time</td>
<td>time to half-area (signal decay measurement)</td>
</tr>
<tr>
<td>0-CROSS</td>
<td>Time</td>
<td>number of times signal crosses zero volts</td>
</tr>
<tr>
<td>25-CROSS</td>
<td>Time</td>
<td>number of times signal crosses ±25% maximum voltage</td>
</tr>
<tr>
<td>1/8T, 2/8T, etc.</td>
<td>Time</td>
<td>normalized time octiles of RMS voltage</td>
</tr>
<tr>
<td>FRQMEAN</td>
<td>Freq.</td>
<td>frequency equal to the mean of the freq. intensities</td>
</tr>
<tr>
<td>FRQMED</td>
<td>Freq.</td>
<td>frequency at mid-area of the integrated freq. intensities</td>
</tr>
<tr>
<td>FRQCREST</td>
<td>Freq.</td>
<td>ratio of maximum power to RMS power</td>
</tr>
<tr>
<td>FQRTLBW</td>
<td>Freq.</td>
<td>bandwidth between the 2\textsuperscript{nd} and 3\textsuperscript{rd} intensity quartiles</td>
</tr>
<tr>
<td>FBW&gt;15%</td>
<td>Freq.</td>
<td>bandwidth of freq. whose intensities &gt; 15% of max.</td>
</tr>
<tr>
<td>DFB1, DFB2, etc.</td>
<td>Freq.</td>
<td>eight user-defined frequency bands</td>
</tr>
</tbody>
</table>
1.4 Oscillating Chemical Reactions

1.4.1 History

The history of the discovery of oscillating chemical reactions can be reliably traced to the early 1900s when A.J. Lotka published a series of papers demonstrating the theory and practice of periodic reactions in a gas-phase system. Soon after, Bray discovered the first liquid-phase example; the iodate-ion catalyzed decomposition of hydrogen peroxide. Liebhafsky joined Bray in an effort to map out the regions of acidity where various reactions predominate, and then to isolate those reactions in order to determine their rate constants. The reaction became known as the Bray-Liebhafsky (BL) oscillator. Due to the instrumental limitations of the period, conclusive data could not be gleaned from this complex system, and it was decades later before interest in oscillating chemical systems was rekindled.

It was in Russia, in 1951, that Belousov uncovered temporal oscillations in the cerium-ion-catalyzed oxidation of citric acid by bromate ion. This work was published in 1958 in the proceedings of a minor radiation medicine conference. Zhabotinskii continued Belousov's work and the reaction became known as the Belousov-Zhabotinskii, or BZ reaction. Unlike previous oscillators, the BZ reaction demonstrated both spatial and temporal periodicity. Supported by recent advances in instrumentation and mathematics, many researchers began studying oscillating reactions.
Figure 1-3. Oscillating reaction publications.
Chapter 1

Burger researched the impact of homogeneous oscillators on the chemical literature\textsuperscript{27} and stated "A scientific revolution took place with the discovery of periodic colour changes in the aqueous mixture of citric acid-bromate ion-cerium ion." Burger's raw data is expressed in graphical form in Figure 1-3.

In a one-page article in the Journal of Chemical Education (1973) two high school teachers, Thomas Briggs and Warren Rauscher, reported an oscillating reaction which "gives striking cyclic changes from colourless to gold to blue using simple reagents."\textsuperscript{28} The reacting solution incorporates the reagents from the Bray-Liebhafsky (BL) oscillator with the addition of an organic substrate (typically malonic acid) and a metal-ion catalyst (usually manganese). Unlike the BL oscillator which requires high temperatures (> 50°C) to oscillate appreciably, the Briggs-Raucher (BR) oscillator runs at a rate of several cycles per minute \textit{at room temperature} after a short induction period.

In 1975, Cooke began the first systematic investigations of the BR oscillator in which each reagent was separately varied and the effect on the oscillation frequency noted\textsuperscript{29}. In 1979, the work was extended to cover the effects of the reagents on all the oscillator's reaction phases: the induction period, waveshape, time periods, and the mode of conclusion\textsuperscript{30}. Few details were provided concerning the mechanism, however, and it was not until 1982 that a plausible skeleton mechanism was published simultaneously by two research groups\textsuperscript{31,32}.

1.4.2 General Theory

Contrary to conventional wisdom, oscillating reactions are quite common, especially in biological systems. In contrast to 'normal' or 'ordinary' chemical reactions, the concentrations of products in an oscillating reaction do not rise smoothly to a maximum. Instead, they exhibit a tendency to rise and fall cyclically. There is some
dispute in the literature as to whether the systems are exhibiting periodic or chaotic behaviour\textsuperscript{33}. However, the kinetic and thermodynamic criteria that a system must meet for oscillations to take place have been defined quite precisely:

- oscillations only occur in systems far from equilibrium
- the variables that determine the reaction rates are coupled kinetically
- oscillating reaction mechanisms contain autocatalytic processes

To study a system far from equilibrium usually requires that the system be open so that energy and/or mass can be exchanged with the outside. Note that this is a characteristic of a biological system, which constantly renews itself by interaction with the outside world. Researchers have duplicated open systems through the use of continuous-flow, stirred-tank reactors (CSTR)\textsuperscript{34}. In a CSTR, reactants are pumped into a rapidly stirred, fixed volume reactor. The partly reacted mixture is drained from the tank at the same rate as fresh reactants are pumped in, hence maintaining a constant volume.

The second condition is the assertion that the concentration of one component will effect the rate of change of concentration of a second component. These two components are then referred to as coupled species.

The third condition is an empirical observation from studying oscillating reactions. It has been found that an oscillating system requires some sort of feedback mechanism in order to function. For example, consider a system in which an enzyme, EH, can undergo either reversible deprotonation:

\begin{equation}
\text{Eqn. 1-2} \quad \text{EH (active) } \rightarrow \text{ E- (inactive) } + \text{ H}^+ \quad \text{rate } K_a
\end{equation}

or may catalytically deprotonate a substrate (SH):

\begin{equation}
\text{Eqn. 1-3} \quad \text{EH + SH } \rightarrow \text{ EH + S' + H}^+ \quad \text{rate } k_2
\end{equation}
If $K_d$ is large, then Eqn. 1-2 initially predominates, producing large amounts of inactive enzyme, leaving little active enzyme for Eqn. 1-3. However, as Eqn. 1-3 proceeds, $H^+$ is generated which drives Eqn. 1-2 to the left, raising the concentration of active enzyme. This in turn increases $k_2$, producing even more $H^+$, and driving the first reaction even further left.

In a closed system, this sequence of steps would continue until the concentration of SH is depleted, or there is sufficient acid to inhibit both processes. In an open system, however, $H^+$ would begin to diffuse out of the reaction volume into regions of lower acid concentration. This will have the effect of Eqn. 1-2’s equilibrium shifting to the right, once more inhibiting the second reaction. Over time, diffusion would replenish SH sufficiently to begin the autocatalytic cycle once more. The system will oscillate between periods of rapid reaction when $[H^+]$, $[SH]$, and $[EH]$ are large, and periods of slow reaction when $[EH]$ and $[SH]$ are low.

In practice, a system of this nature often has two relatively stable states. An oscillating chemical reaction may be thought of as a system which fluctuates between these two states. The feedback in the reaction mechanism is what provides the impetus to keep moving between states rather than settle permanently in a single state.
1.4.3 Briggs-Rauscher Oscillator

1.4.3.1 Reaction Mechanism

From the historical perspective presented earlier, it is apparent that the study of oscillating chemical reactions has enjoyed a rich and lengthy history. From the many publications written pertaining to chemical oscillators based on iodate ion and hydrogen peroxide, there has arisen a pseudo-standard for the labeling of mechanistic steps. Each step is given one of the following labels:

- **Iodine** reactions where there is no net change in oxidation number of iodine
- **Up** reactions where there is a net oxidation of iodine
- **Down** reactions where there is a net reduction of iodine
- **Oxygen** reactions involving oxygen species, with no net change in oxygen oxidation number
- **Manganese** reactions involving the Mn(II) catalyst
- **Carbon** reactions involving the organic substrate

For the purposes of this work, previously published mechanistic steps will use the preceding numbering system. All other mathematical and chemical equations will be numbered sequentially as illustrated by Eqn. 1-2 on page 15.

In describing the BR oscillator, it is helpful to first characterize its predecessor, the BL oscillator. This reaction begins with three deceptively simple reagents: hydrogen peroxide, iodate, and water in mineral acid. Bray was studying this system\(^{22}\) when he happened upon a narrow concentration region where the iodine concentration oscillated slowly with a period of several days. Despite the limited equipment of the period, the base processes were elucidated:
iodine production:
Eqn. 1-4 \[ 5\text{H}_2\text{O}_2 + 2\text{IO}_3^- + 2\text{H}^+ \rightarrow \text{I}_2 + 5\text{O}_2 + 6\text{H}_2\text{O} \]

iodine consumption:
Eqn. 1-5 \[ 5\text{H}_2\text{O}_2 + \text{I}_2 \rightarrow 2\text{IO}_3^- + 2\text{H}^+ + 4\text{H}_2\text{O} \]

The net result of Eqn. 1-4 and Eqn. 1-5 is the catalytic decomposition of hydrogen peroxide:
Eqn. 1-6 \[ 10\text{H}_2\text{O}_2 \rightarrow 10\text{H}_2\text{O} + 5\text{O}_2 \]

These base processes were a starting point for those researchers investigating the BR oscillator. Eqn. 1-4 is the limiting step whose rate is greatly increased by the addition of Mn(II). Furrow and Noyes postulated a free-radical mechanism\(^{32}\) to explain the rate increase:

free radical initiation:
D3. \[ \text{H}^+ + \text{IO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HOIO} + \text{H}_2\text{O} + \text{O}_2 \]
I5. \[ \text{H}^+ + \text{IO}_3^- + \text{HOIO} \rightarrow 2\text{IO}_2^- + \text{H}_2\text{O} \]

chain reaction:
M1. \[ \text{IO}_2^- + \text{H}_2\text{O} + \text{Mn}^{2+} \Leftrightarrow \text{HOIO} + \text{Mn(OH)}^{2+} \]
M2. \[ \text{Mn(OH)}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Mn}^{2+} + \text{HOO}^- \]
D4. \[ \text{H}^+ + \text{IO}_3^- + \text{HOO}^- \rightarrow \text{IO}_2^- + \text{H}_2\text{O} + \text{O}_2 \]

chain termination:
I4. \[ 2\text{HOIO} \rightarrow \text{IO}_3^- + \text{HOI} + \text{H}^+ \]
D1. \[ \text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{O}_2 + \text{H}^+ + \text{H}_2\text{O} \]
I1. \[ \text{HOI} + \text{I}^- + \text{H}^+ \Leftrightarrow \text{I}_2 + \text{H}_2\text{O} \]
The stoichiometry of Eqn. 1-4 can be obtained with \(4(M1) + 4(M2) + 4(D4) + 2(I4) + (D1) + (I1)\). The mechanism for iodine consumption may be explained without resorting to free radicals; unlike the BL system in which \(I_2\) consumption is via reoxidation to iodate, the BR system uses the organic substrate as a convenient halogen sink. Again from Furrow and Noyes:

*enolization and halogen sinking:*

\[
\begin{align*}
\text{C3. } & \text{ RH } \rightleftharpoons \text{ enol} \\
\text{C4. } & \text{ enol } + \text{ I}_2 \rightarrow \text{ RI } + \text{ I}^- + \text{ H}^+ \\
\end{align*}
\]

*production of HOI:*

\[
\begin{align*}
\text{I3. } & \text{ I}^- + \text{ IO}_3^- + 2\text{H}^+ \rightarrow \text{ HOIO } + \text{ HOI} \\
\text{I2. } & \text{ HOIO } + \text{ I}^- + \text{ H}^+ \rightarrow 2\text{HOI} \\
\end{align*}
\]

The presented model is only a skeleton. Experimental rate constants are available for only seven steps, the remaining are estimated or adjusted so as to produce oscillations in the computer models. There is no quantitative agreement between experiment and model. The magnitude of oxygen evolution is unknown. The presence of CO\(_2\) is debatable.

**1.4.3.2 Heat Production**

Cooke’s studies in 1979 included limited heat production data obtained using a thermistor-Wheatstone bridge circuit\(^{30}\). He studied the BR reaction using high H\(_2\)O\(_2\) and low malonic acid concentrations in a 50 mL reaction volume. The resulting temperature-time curves were low-resolution but definitely showed a three degree rise in temperature over the nine minute life of the reaction.
In 1987 Lamprecht and Schaarschmidt conducted microcalorimetric measurements on both the BZ and the BR reactions. For the BR reaction, they reported some ten oscillations with a period of 56 s in the heat production. Unfortunately, all their data was presented in arbitrary units and phase relationships could not be directly established due to the thermal inertia of the calorimeter. In the end they concluded that further details concerning oscillatory heat production may be drawn after time-consuming deconvolution of the calorimeter output.

1.5 CAE and the Briggs-Raucher Iodine Clock

The pressing question is what physical and/or chemical processes in the iodine clock are giving rise to the acoustic activity reported by Betteridge. Since the iodine clock evolves copious amounts of O₂ and bubble evolution is a known source of acoustic emission, it is a reasonable hypothesis that bubble evolution is the primary source of acoustic emission in the iodine clock.

1.5.1 Bubble Nucleation Theory

For the purposes of this work, a bubble may be defined as gas surrounded entirely by a liquid with a working upper diameter of about one millimeter. A bubble may be formed in the bulk of the solution (homogeneous nucleation) and/or at a surface (heterogeneous nucleation). Studies of supersaturated gas/water systems found heterogeneous nucleation to be the dominant mechanism of bubble formation. The degree of dominance depends mainly upon two parameters: contact angle and nucleation site geometry.
A bubble forms at a nucleation site at a given contact angle, characteristic of the gas/liquid system under study, of between 0 and 120°. A contact angle of 0° represents the homogeneous nucleation case where bubble detachment is effectively instantaneous and the overall rate is determined solely by the nucleation kinetics. At contact angles greater than 0° the nucleation kinetics may be dominated by either the nucleation rate or the detachment rate. The literature frequently reports the dimensionless factor $L$ where $L$ is the ratio of the time required for detachment to the time required for nucleation. Hence, when $L < 1$, the nucleation rate dominates and when $L > 1$, the detachment rate dominates. Lubetkin\textsuperscript{14} reported that for an acoustic method to be useful $L$ must be < 1, implying that the contact angle must be close to zero. Lubetkin's study of the CO$_2$/H$_2$O system on glass surfaces found contact angles of less than 5°.

The effect of the nucleation site geometry has not been investigated for the case of supersaturated solutions. For details on the effects in the case of boiling refer to the review of Cole\textsuperscript{38}.

Basic bubble nucleation mathematics theory remains much the same as when it was first proposed in 1939 by Volmer\textsuperscript{39}. The first equation relates the bubble pressure ($P_r$) to the external pressure ($P_{\infty}$), the surface tension ($\sigma$) and the bubble radius ($r$).

$$P_r = P_{\infty} + \frac{2\sigma}{r}$$

Equation 1.7 expresses the concentration of the gas in solution as a product of Henry's Law constant ($\kappa$) and the bubble pressure:

$$C_{\text{soln}} = \kappa P_r$$

If the bubble is not at equilibrium then the bubble will grow by diffusion of gas into it if $P_r < (C_{\text{soln}}/\kappa)$. 
According to Volmer, density fluctuations in a solution create microscopic, short-lived cavities called *embryos*. An embryo must reach a critical radius before bubble nucleation can proceed:

\[
\text{Eqn. 1.8} \quad r_{\text{crit}} = \frac{2\sigma}{C_{ss}/\kappa - P_o}
\]

with \(C_{ss}\) representing the supersaturated gas concentration. The rate of nucleation \(J\) in Volmer's theory is proportional to \(\exp(-W/kT)\) where \(W\) is the work required to expand the embryo into a spherical cavity:

\[
\text{Eqn. 1.9} \quad W = \sigma A - (P_r - P_o)v
\]

where \(A\) is the area and \(v\) the volume. Equations 1.6 through 1.9 may now be combined to form:

\[
\text{Eqn. 1.10} \quad W = \frac{16\pi\sigma^3}{3(C_{soln}/\kappa - P_o)^2}
\]

where it is approximately true that,

\[
\text{Eqn. 1.11} \quad J = \alpha \exp\left(-\frac{\beta}{C_{soln}}\right)^2
\]

where \(\alpha, \beta\) are constants. It can be seen that a large increase in \(J\) will occur when \(C_{soln}\) reaches a critical value.
Chapter Two - Preliminary Studies Using Batch Methods

“...or was it unlock the safe and then swim to the surface?”
- Houdini

2.1 Introduction

This work represents research in an area of analytical chemistry which is still largely unexplored. When the experiments were being planned, the challenge was to set up apparatus which would yield useful chemical information without requiring extensive time or resources to assemble. This was accomplished by putting together instruments from a variety of disciplines and tying them together with software written in-house. This is described in more detail below.
2.2 Experimental

2.2.1 Briggs-Rauscher Chemical System

Two sets of reagents were made up from commercially available chemicals and were used without further purification. Reagent Set A consisted of reagents which were made up to the concentrations recommended by Briggs and Rauscher. Reagent Set B were the same reagents, but the concentrations were reduced by two-thirds. The summary of reagent concentrations can be found in Table 2-1.

The hydrogen peroxide concentration was determined twice daily using titanium(IV) oxalate as described by Sellers\textsuperscript{40}. The starch solution was prepared fresh each day by vigorously boiling the requisite amount of starch in distilled water until the originally clear solution turned translucent, as recommended by Vogel\textsuperscript{41}.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Source and Grade</th>
<th>Reagent Set A Concentration</th>
<th>Reagent Set B Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>BDH, ACS Analytical</td>
<td>1.200 M</td>
<td>0.4000 M</td>
</tr>
<tr>
<td>KIO\textsubscript{3}</td>
<td>BDH, ACS Analytical</td>
<td>0.0529 M</td>
<td>0.0177 M</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>BDH, ACS Analytical</td>
<td>0.0500 M</td>
<td>0.0167 M</td>
</tr>
<tr>
<td>CH\textsubscript{2}(COOH)\textsubscript{2}</td>
<td>Fisher, ACS</td>
<td>0.0670 M</td>
<td>0.0223 M</td>
</tr>
<tr>
<td>MnSO\textsubscript{4}</td>
<td>MacArthur, ACS</td>
<td>0.0067 M</td>
<td>0.0022 M</td>
</tr>
<tr>
<td>starch</td>
<td>BDH, ACS Analytical</td>
<td>0.01% v/v</td>
<td>0.01% v/v</td>
</tr>
</tbody>
</table>
2.2.2 Instrumental System

The instrumental apparatus is illustrated in Figure 2-1. A brief summary of each component's make, model and settings is given in Table 2-2. Information about the manufacturers can be found in Appendix B. The chemical reaction took place in a large, shallow, flat-bottomed Pyrex® dish approximately 15 cm in diameter and 5 cm high. The dish rests upon a large sheet of Styrofoam (not shown for clarity). The center of the Styrofoam has been cut out to accommodate a piezoelectric transducer which is in contact with the dish through a thin layer of acoustic coupling grease. The piezoelectric crystal transduces the chemical acoustic wave into an alternating current (a.c.) electrical signal and amplifies it with an internal 40 dB amplifier. This amplified a.c. signal is then fed into a dual-stage conditioning amplifier. The first stage further amplifies the a.c. signal according to the amount specified by panel-mounted buttons, while the second stage consists of a bandpass filter that rejects those frequencies which fall outside a user-defined range. In this experiment frequencies below 100 kHz and above 2 MHz were excluded. The lower limit was chosen to exclude any possible high-frequency noise (i.e., audible frequencies), while the upper limit was chosen to exclude the range above the transducer's response limit. It should be noted that extremely intense signals (>10 volts) overload the amplifier and allow all frequencies to pass. Thus, the amplification setting was carefully chosen to obtain the best response without the chance of signal overload. The output stage of the amplifier divided the signal into a conditioned a.c signal and a d.c. peak-detect signal with 200 ms time constant. The conditioned a.c. signal was sampled by a digital storage oscilloscope while the d.c. signal was fed directly into an analog chart recorder.
The digital storage oscilloscope was operated in a triggered data acquisition mode. Using this method, the oscilloscope continuously samples the analog signal from the conditioning amplifier, maintaining a small sampling buffer of 32 data points. When the signal breaches a user-defined trigger voltage level, the oscilloscope is said to have been triggered, and it stores the buffered data points (pre-trigger points) as well as the next 992 points into its memory and informs the control computer that a signal has been detected.

Table 2-2. Apparatus list for batch studies.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Settings/Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>paddle stirrer</td>
<td>Fisher</td>
<td>92a</td>
<td>stainless steel</td>
</tr>
<tr>
<td>piezoelectric transducer</td>
<td>Brüel &amp; Kjær</td>
<td>8312</td>
<td>40 dB gain</td>
</tr>
<tr>
<td>conditioning amplifier</td>
<td>Brüel &amp; Kjær</td>
<td>2638</td>
<td>40 dB gain, 100 - 2000 kHz filter</td>
</tr>
<tr>
<td>digital storage oscilloscope</td>
<td>Tektronix</td>
<td>T2430a</td>
<td>8 mV resolution, 2.50 MHz samp.freq.</td>
</tr>
<tr>
<td>chart recorder</td>
<td>BBC</td>
<td>SE120</td>
<td>6 cm/min., 500 mV full scale</td>
</tr>
<tr>
<td>personal computer</td>
<td>Campus Computers</td>
<td>386/20</td>
<td>GPIB interface used for communication with scope</td>
</tr>
</tbody>
</table>
acquired and is awaiting transfer. It is now the responsibility of the control computer to initiate signal transfer, store the signal (1024 points total) onto disk for post-processing, and re-arm the oscilloscope.

The control computer was an IBM PC-AT compatible personal computer with an Intel 80386 processor. It communicated with the oscilloscope via the industry-standard GPIB interface. Software written in-house by this author was used to control the oscilloscope’s initial operating parameters. While the experiment was underway, the software was responsible for arming the oscilloscope and then retrieving the signal it acquired once triggered. This arm-trigger-transfer sequence was repeated until the operator deemed the experiment should be concluded. For more automated experiments, the software could be instructed to terminate signal acquisition after a user-defined period of time had elapsed or a particular number of signals acquired.

2.2.3 Timing and Methods

Strict timing control is necessary in order to reproducibly capture the oscillating iodine clock’s unique temporal behaviour. A method was needed to deliver accurate amounts of reagent to the reaction vessel in a timely reproducible manner while simultaneously starting the recording equipment. To this end the reagents were premixed as three separate solutions. Solution #1 contained peroxide, solution #2 comprised the iodate and sulfuric acid, and solution #3 the malonic acid, starch and manganese. Without the catalyst, the reaction proceeds slowly at room temperature and so 25 mL of each solution was pipetted into the reaction vessel in its numerical order.

Once all three solutions had been delivered, the paddle stirrer was started along with the oscilloscope and chart recorder. Several trial runs were conducted for timing purposes and it was noted that oscillations ceased after approximately 150 seconds. The
progress of experiments was monitored and data collection halted after 300 seconds. Colour changes in the solution were observed visually and recorded manually. This experimental sequence was repeated five times for each reagent set.

2.2.3.1 Stirring Effects

Briggs and Rauscher reported in their 1973 paper that “Constant stirring improves the cycling, but is not essential.” While no detailed study on the effects of stirring in the BR oscillator has been published, Dutt and Menzinger did report on the effect of stirring and temperature on a Belousov-Zhabotinskii-like reaction. They concluded that increased stirring increased both the induction and oscillation periods and that the greatest effects were observed at low temperatures of ca. 15°C.

As mentioned in the previous section, a paddle stirrer was used in these experiments to provide mixing. Since the paddle stirrer operated at a fixed speed, and the experiments were conducted at room temperature, we make the assumption that stirring effects are constant between replicate runs.

2.2.3.2 Sampling Frequency

In this experiment there are two sampling frequencies to be considered. First, there is the rate at which the oscilloscope samples the analog a.c. signal which can be set either manually or through computer control. The piezoelectric transducer has an upper limit frequency response of ≈ 1 MHz, so a sampling frequency of 2.5 MHz was selected to avoid aliasing. The second sampling rate requires greater explanation.

In a triggered data acquisition mode, the oscilloscope, once triggered, is idle while it waits for a re-arm command. The control computer does not issue the re-arm instruction until it has received and stored the digitized signal from the oscilloscope.
Thus, the signal transfer process is the rate-limiting step in the data acquisition cycle. The period of the limiting step is the longest of one of these three events: (i) the oscilloscope’s data transfer to the GPIB interface, (ii) the GPIB’s data transfer to the control computer or (iii) the control computer’s data transfer to its internal hard disk. Measurements have determined the first event, data transfer to GPIB interface, is the limiting step, requiring approximately 0.8 seconds.

2.2.4 Sensor Calibration

As mentioned in Chapter One, the chemical acoustic wave may undergo several transformations and attenuations before arriving at the piezoelectric sensor. Thus, the sensor must be secured to the reaction vessel in a manner both reproducible and allowing transfer of maximum signal amplitude. To this end, a computer-controlled signal generator (model PCIP-SST, Metrabyte Corp.), with built-in calibration, was purchased. The device, a "signal generator on an adapter card", was placed in one of the expansion slots of an IBM PC-AT compatible computer.

Figure 2-2 illustrates the calibration procedure. The output of the signal generator was connected to a flat-response transducer (model FAC500, AET Corp.) to be used as a sound source. The transducer was securely contacted to the reaction vessel and coupled through a thin layer of acoustic grease. Instead of the reaction mixture in the vessel, an equivalent volume of distilled water was used to ensure a nearly identical mass loading on the transducer. This is possible since the sulfuric acid in the reaction mixture is present at less than 1% by weight, having a density of 1.0051 g/mL, which is comparable to distilled water. Calibrations were performed with and without the paddle stirrer in place to determine if the mixing gave rise to an acoustic signature.
The signal generator was programmed to step through a range of frequencies from 100 kHz to 2 MHz at a known output voltage. The test signals were captured and processed as if during an actual experiment. The resulting power spectra were compared to those captured during earlier runs to see if the transducer response had changed.

Stirring effects were not observed in the averaged power spectra, and the transducer response remained unchanged over the time period the experiments were conducted, in agreement with the work of Wentzell\textsuperscript{44}.

![Diagram](image)

Figure 2-2. Apparatus for calibration procedure developed for batch studies.

### 2.3 Discussion

An experiment of this nature yields a large volume of data. First there are the raw a.c. signals which have been pre-processed by the conditioning amplifier before digitization. Consider that one digitized signal is 1024 data points of information, each
one byte in length, and that more than 300 signals are captured during the course of a five minute experiment. An average run thus produces more than 307,000 bytes of raw data; a considerable amount of information to be processed and analyzed. There is also the d.c. signal output from the conditioning amplifier and recorded by the chart recorder. At a chart rate of 6 cm/min., 30 cm of chart output is generated for every experiment which is a total of 300 cm for these batch studies.

An adequate data reduction and analysis strategy is required. Over the years this research has been conducted, we have attempted to devise efficient and robust data analysis protocols which yield useful chemical information. We begin by considering the d.c. signal data separately from the a.c. signal data.

2.3.1 Analysis of D.C. Signals

For the purposes of this discussion we randomly pick two of the five replicates for Reagent Set A and one of the five replicates for Reagent Set B. Oscillations as evidenced by colour changes were observed for the former reagent set and recorded manually. No oscillations were observed for the latter reagent set. Gas evolution was observed in all experiments, albeit more vigorous during the Reagent Set A experiments.

The relationship between the colour changes and the acoustic emissions is illustrated in Figure 2-3. When the CAE is at a minimum, the solution is colourless. As the solution slowly changes from colourless to gold, there is a corresponding rise in the CAE until a sharp transition to blue is observed at which time the CAE is at a maximum. The solution remains blue until the CAE has once again reached a minimum. The figure is drawn to emphasize all the features. From the experimental data, it can be seen that the peaks are skewed to the right. This is discussed in greater detail in Chapter Three.
The figures C-1 through C-3 are the scanned images of the original chart recordings from the selected experiments. They show acoustic emission intensity as a function of time. The first two figures (Figures C-1 and C-2) have similar features, and we will discuss these at length in the following paragraphs. Figure C-3 is nearly flat indicating that if the oscillating reaction did take place it was not detectable from the d.c. signal at the chosen amplification level.

Figure C-1 is the chart recording of the first run of Reagent Set A. Special attention should be directed to the axes of the recording. Due to the nature of the experimental setup, the horizontal axis is time (increasing left to right), while the vertical axis is voltage which increases from top to bottom. That is, the 0,0 point is the upper left
of the image. The recording itself is straightforward. There is an initial induction phase which rises quickly to a maximum (ca. 22 seconds) before triggering a series of oscillations. Each successive oscillation is attenuated and gains more fine structure until oscillations can no longer be clearly distinguished (ca. 150 seconds). There is also a general increase in signal intensity until ca. 270 seconds, after which a decreasing trend is noticeable.

Figure C-2, the chart recording of the second run of Reagent Set A, exhibits similar features. A steep induction phase (ca. 22 seconds), increasingly attenuated oscillations to ca. 140 seconds, and finally a decreasing trend after ca. 180 seconds.

The fine structure of the chart recordings makes it difficult to isolate key phases. To improve the image quality, the chart recordings for Reagent Set A were digitized and then smoothed with a 15% FFT algorithm (see Glossary). The results for the first 150 seconds (when oscillations occur) are in Figure C-4. From this figure we will discuss the following phases: induction, positive slope (pos), negative slope (neg), and shoulder. Induction represents the initial phase of the reaction before oscillations commence. A pos phase is when d(response)/dt is positive, neg when d(response)/dt is negative and shoulder represents a sudden decrease in the magnitude of d(response)/dt without changing sign.

Table 2-3 lists the time periods for each phase. The data indicate remarkable synchronicity between the two runs until the third oscillation at which time synchronicity is lost on the neg phase. When the phases are sorted as in Table 2-4, other trends become apparent. These trends are discussed in detail below.
Table 2-3. Phases present in Reagent Set A data, sorted by time

<table>
<thead>
<tr>
<th>Phase</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>Stop</td>
<td>Dur</td>
</tr>
<tr>
<td>Induction</td>
<td>0</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Neg</td>
<td>22</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>Pos</td>
<td>30</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>Neg</td>
<td>35</td>
<td>48</td>
<td>13</td>
</tr>
<tr>
<td>Pos</td>
<td>48</td>
<td>54</td>
<td>6</td>
</tr>
<tr>
<td>Neg</td>
<td>54</td>
<td>61</td>
<td>7</td>
</tr>
<tr>
<td>Shoulder</td>
<td>61</td>
<td>66</td>
<td>5</td>
</tr>
<tr>
<td>Pos</td>
<td>66</td>
<td>73</td>
<td>7</td>
</tr>
<tr>
<td>Neg</td>
<td>73</td>
<td>81</td>
<td>8</td>
</tr>
<tr>
<td>Shoulder</td>
<td>81</td>
<td>86</td>
<td>5</td>
</tr>
<tr>
<td>Pos</td>
<td>86</td>
<td>92</td>
<td>6</td>
</tr>
<tr>
<td>Neg</td>
<td>92</td>
<td>102</td>
<td>10</td>
</tr>
<tr>
<td>Shoulder</td>
<td>102</td>
<td>108</td>
<td>6</td>
</tr>
<tr>
<td>Pos</td>
<td>108</td>
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</tr>
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<td>Neg</td>
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<tr>
<td>Shoulder</td>
<td>125</td>
<td>135</td>
<td>10</td>
</tr>
</tbody>
</table>
Table 2-4. Phases present in Reagent Set A data, sorted by phase.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Run 1 Start</th>
<th>Run 1 Stop</th>
<th>Run 1 Dur</th>
<th>Run 2 Start</th>
<th>Run 2 Stop</th>
<th>Run 2 Dur</th>
<th>Notes (all times in seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neg</td>
<td>22</td>
<td>30</td>
<td>8</td>
<td>22</td>
<td>30</td>
<td>8</td>
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<tr>
<td>Neg</td>
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<td>13</td>
<td>35</td>
<td>48</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Neg</td>
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<td>61</td>
<td>7</td>
<td>54</td>
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<td>7</td>
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<td>125</td>
<td>9</td>
<td>116</td>
<td>125</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Induction</td>
<td>0</td>
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<td>22</td>
<td>0</td>
<td>22</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Shoulder</td>
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<td>66</td>
<td>5</td>
<td>61</td>
<td>66</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Shoulder</td>
<td>81</td>
<td>86</td>
<td>5</td>
<td>80</td>
<td>86</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Shoulder</td>
<td>102</td>
<td>108</td>
<td>6</td>
<td>98</td>
<td>106</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Shoulder</td>
<td>125</td>
<td>135</td>
<td>10</td>
<td>125</td>
<td>132</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Pos</td>
<td>30</td>
<td>35</td>
<td>5</td>
<td>30</td>
<td>35</td>
<td>5</td>
<td>osc. #1</td>
</tr>
<tr>
<td>Pos</td>
<td>48</td>
<td>54</td>
<td>6</td>
<td>48</td>
<td>54</td>
<td>6</td>
<td>osc. #2</td>
</tr>
<tr>
<td>Pos</td>
<td>66</td>
<td>73</td>
<td>7</td>
<td>66</td>
<td>73</td>
<td>7</td>
<td>osc. #3</td>
</tr>
<tr>
<td>Pos</td>
<td>86</td>
<td>92</td>
<td>6</td>
<td>86</td>
<td>92</td>
<td>6</td>
<td>osc. #4</td>
</tr>
<tr>
<td>Pos</td>
<td>108</td>
<td>116</td>
<td>8</td>
<td>106</td>
<td>116</td>
<td>10</td>
<td>osc. #5</td>
</tr>
</tbody>
</table>

2.3.1.1 Induction phase

The emphasis of previous research has been on the mechanism of the oscillations or the effect of different reagents or physical factors. In the literature there is little discussion of the induction phase. Cooke\textsuperscript{29} briefly mentioned that "under suitable
Chapter 2  Preliminary Studies Using Batch Methods

conditions the oscillations are preceded by an induction period”. He also systematically varied the concentrations of the various reagents and measured their effect on the induction phase. He concluded that the rate of I₂ production is first order in [H₂O₂] and independent of the other species in the following reaction:

Eqn 2-1    \[ 2I_2O_3^- + 5H_2O_2 + 2H^+ \rightarrow 5O_2 + I_2 + 6H_2O \]

This provides a starting point from which we can investigate the kinetics of the induction phase based on the chemical acoustic emission data. To this end a plot of LN(Response_adj) versus Time was constructed and can be seen in Figure 2-4 (bottom). The response_adj was computed by subtracting the CAE response (from Figure C-2) from the value for infinite-time CAE. This value was calculated by fitting the data from Figure 2-4 (top) to a single exponential function. It is readily apparent that there are two processes taking place in the induction period. There is a rapid, almost exponential rise for the first five seconds, followed by a less rapid nearly linear rise. These processes can be explained by the following model:

\[ X \rightarrow_{k_1} O_2 (soln) \rightarrow_{k_2} \text{Nucleation} \]

where X is some process which evolves oxygen into solution at rate k₁ (such as Eqn 2-1), followed by bubble nucleation at occurring at rate k₂. The rate law would then be:

Eqn 2-2    \[ \frac{d[O_2]}{dt} = k_1X - k_2[O_2] \]

the concentration of oxygen in solution would quickly build to a steady state:

Eqn 2-3    \[ \frac{d[O_2]}{dt} = k_2[O_2]_{ss} - k_2[O_2] \]

Eqn 2-4    \[ \frac{d[O_2]}{dt} = k_2([O_2]_{ss} - [O_2]) \]
which upon integration

Eqn 2-5 \[ [O_2] = [O_2]_a (1 - \exp(-k_2 t)) \]

Recall from Chapter One that the nucleation rate \( J \) is itself a function of \([O_2]_{\text{soln}}\).

Eqn 2-6 \[ J = \alpha \exp\left(-\frac{\beta}{[O_2]_{\text{soln}}}\right) \]

Lubetkin pointed out in his work\textsuperscript{14} that the rate of nucleation (\( J \)) is closely correlated with the rate of bubble bursting at the free liquid surface. Both Lubetkin’s study and earlier work by Wade\textsuperscript{6} indicate that the bursting is the most likely acoustically emissive process, which ties nucleation to CAE. But how is \( k_2 \) related to \( J \)? As demonstrated in Chapter One, \( J \) is a complex function of many variables and which suggests that no simple relationship between \( k_2 \) and \( J \) may exist, which implies that there is no simple relationship between \( k_2 \) and CAE.
Figure 2-4. Plots of Response vs Time (top) and LN(Response_{adj}) vs Time (bottom).
2.3.1.2 Negative Slope (neg) Phase

For the purposes of this discussion, we define a *neg* phase as one in which 
\( \frac{d(\text{response})}{dt} \) has a negative slope, indicating the rate of acoustic emission is decreasing. Colour provides some indication of the dominant processes. Blue is observed when iodine complexes with starch. The iodide ion gives a colourless solution. Roux and Vidal\textsuperscript{52} noted that a gold colour is observed for the tri-iodide ion.

During a *neg* phase, the colour is observed to change from deep blue to colourless, from which we can infer that:

*i)* \([I_2]\) is decreasing to a minimum.

*ii)* \([I^-]\) rapidly increases to a maximum. (iodide/iodine ratio not favourable to form significant amounts of tri-iodide ion).

For ease of comparison, the *neg* phases are grouped together in Table 2-4 on page 35. The phase durations are not informative. If the phase immediately following the induction phase is discounted as a “transition phase”, then there is a general trend towards decreasing durations. More useful information can be gleaned from the slopes of the lines (Table 2-5). The rate of each *neg* phase is constant until the third oscillation implying that some unknown event occurred which disrupted the reaction at that point. The rate then decreases slightly. The reasonable conclusion is that the rate of acoustic emission during a *neg* phase is independent of the reagent concentrations.
Table 2-5. Neg phase slopes for Run 1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neg (after induction)</td>
<td>-10.0</td>
</tr>
<tr>
<td>Neg (osc #1)</td>
<td>-10.0</td>
</tr>
<tr>
<td>Neg (osc #2)</td>
<td>-10.0</td>
</tr>
<tr>
<td>Neg (osc #3)</td>
<td>-9.4</td>
</tr>
<tr>
<td>Neg (osc #4)</td>
<td>-9.4</td>
</tr>
<tr>
<td>Neg (osc #5)</td>
<td>-9.4</td>
</tr>
</tbody>
</table>

2.3.1.3 Positive Slope (pos) Phase

A *pos* phase is one in which \( d(\text{response})/dt \) has a positive slope, indicating the rate of acoustic emission is increasing. Once again, colour provides some indication of the dominant processes. During a *pos* phase, the colour is observed to change from colourless to gold to deep blue at the peak, from which we can infer that:

1. \([I_2]\) is increasing to a maximum
2. \([\Gamma]\) is low, then builds rapidly

For ease of comparison, the *pos* phases are grouped together in Table 2-4. The slopes of the lines can be found in Table 2-6. A plot of \(1/(Pos \text{ rates})\) vs Event Number is depicted in Figure 2-5. The resulting correlation coefficient was 0.945. The reaction step representing a *pos* phase might be:

\[
D1. \quad \text{HOI} + H_2O_2 \rightarrow \Gamma^- + O_2 + H^+ + H_2O
\]

Second order kinetics suggests that the rate of oxygen evolution is first order in both hypo-iodous acid and hydrogen peroxide.
Table 2-6. Pos phase slopes for Run 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pos (after induction)</td>
<td>28.0</td>
</tr>
<tr>
<td>Pos (osc #1)</td>
<td>17.5</td>
</tr>
<tr>
<td>Pos (osc #2)</td>
<td>15.3</td>
</tr>
<tr>
<td>Pos (osc #3)</td>
<td>14.0</td>
</tr>
<tr>
<td>Pos (osc #4)</td>
<td>13.3</td>
</tr>
<tr>
<td>Pos (osc #5)</td>
<td>11.4</td>
</tr>
</tbody>
</table>

Figure 2-5. Fit of $1/(\text{Pos phase rates})$ vs. Event Number

$r^2 = 0.945$
2.3.1.4 Shoulder Phase

The most interesting feature of the shoulder phase is that it is unreported in the literature and hence may be unique to chemical acoustic emission. Published figures showing oscillations in iodine species generally consist of saw-tooth or sinusoidal traces depending upon the mineral and/or malonic acid concentrations\(^{29}\). The oscillations then terminate abruptly or gradually damp away.

The data collected in this work clearly shows formation of a shoulder beginning with the second oscillation and increasing in size and duration until oscillations are no longer distinguishable. Does this represent a process which can only be detected via chemical acoustic emission? If so, what is the process?

To answer these questions, attention must be drawn to the reactions occurring during the neg phase. It was suggested above that the following is happening:

\[ i) \quad [I_2] \text{ is decreasing to a minimum} \]
\[ ii) \quad [I^-] \text{ is increasing to a maximum} \]

Recall from the introduction in Chapter One that iodine is consumed during halogen sinking by the organic substrate:
\[
C_4\text{. enol} + I_2 \rightarrow RI + I^- + H^+ 
\]
and subsequently produces iodos and hypo-iodous acid:
\[
I^- + IO_3^- + 2H^+ \rightarrow HOIO + HOI 
\]

These reactions, as well as further catalyzed production of HOIO, continue until the concentrations of HOIO and \( I^- \) reach a critical level. When reached, a “switch is thrown” and the oscillator begins consuming HOIO and \( I^- \) (Eqn 12, to form HOI) rather
than producing them. On the chart recordings, the switch is represented as the sudden transition from a negative slope to a positive one. A shoulder appears to be a phenomenon whereby just as the reactants reach the critical level required to throw the switch, there is a sudden reversal of one of the producing reactions, and production becomes slightly delayed. Another possibility is that the switch has been thrown in the “forward” direction, only to be thrown “backward” again only a few seconds later. The latter explanation appears to fit better when the shoulders of the terminal oscillations are examined. Clearly, there is a tendency for the shoulder to rise as if it were a pos phase, only for it to come back down to its previous response level. Chemically, the processes behind the shoulder phase are difficult to explain. One possibility may lie in the concentration of H₂O₂.

When the “switch is thrown” there begins autocatalytic production of hypo-iodous acid:

I2. \( \text{HOIO} + \text{I}^- + \text{H}^+ \rightarrow 2\text{HOI} \)
D1. \( \text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{O}_2 + \text{H}^+ + \text{H}_2\text{O} \)

As the concentration of H₂O₂ decreases, reaction D1 may proceed too slowly to keep up with reaction I2, and so HOIO and I⁻ will not be able to produce sufficient HOI before falling below their critical levels. The switch is then “reversed” and the oscillator continues.
2.3.2 Analysis of A.C. Signals

A data analysis strategy for processing CAE signals was outlined in Chapter 1, and will be followed here.

2.3.2.1 Signal Validation

The step immediately following signal acquisition is signal validation. The program AESCHECK was used to remove those signals which were over-ranged or captured as a result of under-triggering.

2.3.2.2 Signal Analysis

Signal classes (italics) were assigned based on the events observed and discussed above:

"indu" - if the signal was captured during the Induction phase
"negs" - if the signal was captured during a Negative Slope (neg) event
"poss" - if the signal was captured during a Positive Slope (pos) event
"shou" - if the signal was captured during a Shoulder event
"none" - if the signal was captured after events could be positively assigned

Class assignments were made only for Reagent Set A experimental runs. For Reagent Set B runs, all signal classes were set to "none".

2.3.2.3 Time Series Analysis

The program TRAPS was initially used to compute the averaged power spectra (AVP) of all the signals captured. Following that, TRAPS computed the AVP of those
signals assigned to each of the four classes mentioned above. The raw signal data were transformed with a Welch window before the fast Fourier transform was applied. The resulting power spectra were then smoothed with a 10% FFT smoothing algorithm.

![Reagent Set B Averaged Power Spectrum](image)

Figure 2-6. AVP of Reagent Set B.

The results for Reagent Set B are shown in Figure 2-6, on the same scale as the AVPs to follow (for ease of comparison). It is very difficult to make out any distinct peaks. The most easily identified peaks are typically those due to the piezoelectric transducer’s unique response signature. The transducer used in this study generates peaks at 786 and 1008 kHz. These peaks are difficult to see in Figure 2-6, but are visible if the y-axis is adjusted as in Figure 2-7.

The magnified view offered by Figure 2-7 reveals more detailed structure of the AVP. There appears to be some acoustic activity as evidenced by the region from 100 to 600 kHz. Recall from the experimental section of this chapter that background noise is mostly eliminated by setting a trigger level voltage about the background noise level, leaving the conclusion that any significant intensity must be from chemical acoustic
activity. The key words here are “significant intensity”. It is too early in the analysis to determine if relative intensities < 0.002 are significant.

![Reagent Set B](image)

**Figure 2-7. AVP of Reagent Set B, with expanded Y axis.**

The results for Reagent Set A, Run 1 are depicted in Figure 2-8. The top graph is the AVP of all the CAE signals collected. The lower four graphs are the AVPs of those signals which fall during the labeled event periods. Those spectra may be tentatively divided into two distinct regions. The first, from 100 to 700 kHz, may be thought of as the “reaction activity” region. The second, from 700 to 1200 kHz, is the “transducer signature” region. In the reaction activity region, each graph shows a prominent peak at 500 kHz which corresponds to earlier studies conducted in this lab and published elsewhere. As it is unreported in other acoustically active chemical systems, it may be a peak characteristic of bubble evolution in the iodine clock reaction.

The first half of the reaction activity region, Figure 2-9, contains those peaks and peak intensities unique to a particular class. Of the four signal classes represented, the induction period is the most unique, exhibiting two major peaks at 125 and 293 kHz. The
remaining classes have three peaks which are similar in frequency but quite different in intensity. They are summarized in Table 2-7. Given the experimental system's frequency resolution of approx. 2.5 kHz, there is significant correlation between the peaks in each event.

Figure 2-8. AVP of Reagent Set A, Run 1
With the exception of the induction period, it is extremely difficult to separate the events via frequency shifts in the reaction activity region of the averaged power spectra. The peak intensities offer some useful information. Peak #1 steadily decreases between events, while peaks #2 and #3, increase then decrease again. Note that if the shoulder event is not present (as in the early oscillations), then all three peaks follow the same decreasing trend.

![Graphs showing relative intensity vs. frequency for induction, negative slope, shoulder, and positive slope](image_url)

Figure 2-9. Reaction activity region of Reagent Set A, Run 1.

The transducer’s signature region is readily identified from Figure 2-8 on page 47. There is little or no reaction activity in this region and the transducer’s signature peaks of 786 and 1008 kHz are easily discernible.
Chapter 2 Preliminary Studies Using Batch Methods

The results for Reagent Set A, Run 2 are depicted in Figure 2-10. Similar to Figure 2-8 above, the top graph is the AVP of all the CAE signals collected and the lower four graphs are the AVPs of those signals which fall during the labeled event periods.

Of the four signal classes represented in the reaction activity region (Figure 2-11), the induction period is no longer unique, exhibiting three major peaks at 125, 210 and 310 kHz, similar to the remaining classes which also have three peaks located near those frequencies.

Table 2-7. Summary of peaks in reaction activity region of Run 1.

<table>
<thead>
<tr>
<th>Event</th>
<th>Peak 1 Freq. (kHz)</th>
<th>Peak 1 Rel. Int. (x10^5)</th>
<th>Peak 2 Freq. (kHz)</th>
<th>Peak 2 Rel. Int. (x10^5)</th>
<th>Peak 3 Freq. (kHz)</th>
<th>Peak 3 Rel. Int. (x10^5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative Slope</td>
<td>125</td>
<td>437</td>
<td>200</td>
<td>370</td>
<td>288</td>
<td>419</td>
</tr>
<tr>
<td>Shoulder</td>
<td>125</td>
<td>415</td>
<td>195</td>
<td>458</td>
<td>288</td>
<td>453</td>
</tr>
<tr>
<td>Positive Slope</td>
<td>127</td>
<td>300</td>
<td>198</td>
<td>401</td>
<td>291</td>
<td>386</td>
</tr>
</tbody>
</table>
Figure 2-10. AVP of Reagent Set A, Run 2.
Figure 2-11. Reaction activity region of Reagent Set A, Run 2.
2.3.2.4 Descriptor Extraction and Analysis

Referring to the CAE data analysis road map which was detailed in Chapter 1, the next step in the analysis of CAE signals is to extract descriptors from the raw signal data. The program FEATURES was used to accomplish this task. Default settings were used with the following exceptions:

- a Welch window transform was applied to the signal data before Fourier transformation
- the bandwidth for computations was limited to the frequency response bandwidth of the transducer which is approximately 100 - 1200 kHz

Since it is impossible to capture every CAE signal emitted by the chemical system, each signal represents a sample from a much larger population. Thus a signal’s descriptors are also a sample of a larger population. Before chemometric tests can be applied, some knowledge of the distribution of values is important. For example, if statistical methods based on normal (Gaussian) distributions are applied to non-Gaussian data, the methods may yield erroneous results leading to faulty conclusions. Reasons why non-Gaussian distributions are obtained may include heterogeneity of samples, rounding off error, and measurements near the detection limit.45 When a Gaussian distribution cannot be obtained, one can use methods which do not require assumptions about the distribution.

One method of determining the type of sample distribution involves dividing the values into a discrete number of buckets, which are then displayed as a histogram. The naked eye can then be used to judge the symmetry of the resulting graph. This method is reliable yet time-intensive. The program DESTREND implements this method.
Descriptor distributions may be viewed on the display screen or the data dumped to disk for later plotting. Processing of the data from Reagent Sets A and B revealed that the majority of descriptors exhibited non-Gaussian distributions.

One of the goals of this chapter is to correlate the visual colour changes with CAE data. Since no colour changes were observed during the Reagent Set B experiments, it is reasonable to form the hypothesis that the Reagent Set B descriptors have different distributions than the Reagent Set A descriptors. A second likely hypothesis is that Runs 1 and 2 of Reagent Set A should have similar descriptor distributions. Due to the non-Gaussian nature of the data, the Wilcoxon two-tailed rank sum test was used to test our hypotheses. This non-parametric test is described in Siegel. The results are tabulated below. Values of less than 1.96 indicate distributions which overlap. Only 4 of 26 descriptors have overlapping distributions when comparing Reagent Set A with B, while 16 of 26 descriptors have overlapping distributions when comparing Runs 1 and 2 of Reagent Set A.

Table 2-8. Results of Wilcoxon Test (Reagent Sets A vs. B)

<table>
<thead>
<tr>
<th>Descriptor</th>
<th>Z Score</th>
<th>Descriptor</th>
<th>Z Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/8 T</td>
<td>-0.91</td>
<td>3/8 T</td>
<td>0.35</td>
</tr>
<tr>
<td>4/8 T</td>
<td>0.32</td>
<td>4/8 T</td>
<td>1.52</td>
</tr>
<tr>
<td>5/8 T</td>
<td>-1.41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2-9. Results of Wilcoxon Test for Reagent Set A. (run 1 vs. 2)

<table>
<thead>
<tr>
<th>Descriptor</th>
<th>Z Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crest</td>
<td>1.91</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>1.42</td>
</tr>
<tr>
<td>t@area/2</td>
<td>-0.99</td>
</tr>
<tr>
<td>0-Cross</td>
<td>0.71</td>
</tr>
<tr>
<td>1/8 T</td>
<td>1.32</td>
</tr>
<tr>
<td>2/8 T</td>
<td>-0.98</td>
</tr>
<tr>
<td>3/8 T</td>
<td>0.24</td>
</tr>
<tr>
<td>4/8 T</td>
<td>0.61</td>
</tr>
<tr>
<td>5/8 T</td>
<td>0.17</td>
</tr>
<tr>
<td>6/8 T</td>
<td>0.27</td>
</tr>
<tr>
<td>7/8 T</td>
<td>-0.17</td>
</tr>
<tr>
<td>8/8 T</td>
<td>-0.85</td>
</tr>
<tr>
<td>Frq Med</td>
<td>1.05</td>
</tr>
<tr>
<td>Frq Mean</td>
<td>-0.95</td>
</tr>
<tr>
<td>DFB4</td>
<td>-0.79</td>
</tr>
<tr>
<td>DFB7</td>
<td>-1.31</td>
</tr>
<tr>
<td>DFB8</td>
<td>1.32</td>
</tr>
</tbody>
</table>
2.3.2.5 Principal Components Analysis

Principal components analysis (PCA), described briefly in Chapter One, was used to reduce the multi-dimensional descriptor data into three dimensions. The data were first autoscaled before used as input to the program PCA. The resulting eigenvectors were rotated with a normal varimax algorithm. The resulting plots showed a cluster with a skewed centroid and no appreciable pattern.

2.3.2.6 Clustering

The primary purpose of clustering data is to determine if there is a statistical basis for the classification of the data. For the purposes of CAE data, the presence of distinct clusters may indicate that the CAE is due to unique acoustic processes. In this study, there is the advantage that classes have already been assigned to signals based on the phases observed in the d.c. data. Hence, clustering may be used to provide statistical weight to the classes already assigned.

The program K-MEANS was used to execute the non-hierarchical K-means algorithm\(^\text{47}\). The descriptor files were first trimmed to remove any CAE signals which could not be classified according to the observed d.c. phases. In practice, this meant removing all signals whose time stamp was greater than 150 seconds. The resulting descriptors were autoscaled before clustering. Since four classes had been previously assigned (induction, negative slope, positive slope, and shoulder) the program K-MEANS was instructed to separate the data into the best four clusters.

One drawback to clustering experimental data is that the number of clusters must be chosen carefully, preferably with a priori knowledge of the system under study. When
limited information is available, some method is needed to review the results to make sure they are reasonable. In the case of CAE data, we can exploit the frequency content of the signals to fulfill this role by computing the averaged power spectrum of each cluster and comparing it with the other clusters. If two clusters exhibit a power spectrum with similar peaks then it is reasonable to assume that the clustering algorithm has subdivided a large cluster into two smaller ones.

In this work, the program TRAPS was used to compute the AVPs of each of the four classes assigned by K-MEANS. The results for Reagent Set B are shown in Figure 2-12. The numbers located in the upper right of each graph indicate the number of signals belonging to that class and the percentage of signals compared to the total. The graph titled “none” represents the power spectrum of those signals which occurred after visible oscillations (i.e. after 150 seconds).

It is evident for this reagent set that class 1 and class 4 are similar and class 2 and class 3 are similar leading to the conclusion that there are only two distinct classes present. The first class (from class 1 and 4) shows a typical power spectrum for noise or background signals and makes up 20% of the classified signals and 10% of the total signals. The second class (from class 2 and 3) is low intensity but dominant, which explains its similarity to the power spectrum for the unclassified signals.
Figure 2-12. Power spectra of K-Means clustering results for Reagent Set B.
2.4 Conclusions

Analysis of the d.c. signal has allowed the oscillating iodine clock reaction to be classified into four distinct phases: *induction phase*, *negative slope phase*, *positive slope phase* and the *shoulder phase*.

In the *induction phase* it is apparent that there are two processes taking place which may be attributed to the following model:

\[
X \xrightarrow{k_1} O_2\text{(soln)} \xrightarrow{k_2} \text{Nucleation}
\]

following the rate law:

\[
\frac{d[O_2]}{dt} = k_1 X - k_2[O_2]
\]

which upon integration yields

\[
[O_2] = [O_2]_{ss}(1 - \exp(-k_2 t))
\]

Following the lead of Lubetkin\(^{14}\), one would expect the acoustic emission intensity to be closely correlated to

\[
k_2[O_2]_{ss}(1 - \exp(-k_2 t))
\]

The *negative slope phase*, when \(I_2\) is decreasing and \(I\) increasing, appears to be independent of reagent concentration. It is difficult to state this as fact on the basis of the limited experimental data at this point. The following chapters will explore this further.

The *positive slope phase*, when both \(I_2\) and \(I\) are increasing, could not be fit closely to a standard rate law. The best fit was to a second order rate law in which it was suggested that the rate of oxygen evolution was first order in both hypo-iodous acid and hydrogen peroxide.
The shoulder phase was the most challenging to explain as it is unreported in the literature and hence may be unique to chemical acoustic emission. A shoulder phase occurs when the oscillator experiences difficulty switching from one state to another.

In the a.c. signal analysis section, time-series analysis of the reaction phases provided the basis for dividing a power spectrum into two distinct regions: the “reaction activity” region and the transducer signature region.

Multivariate statistics yielded mixed results. The majority of the descriptors belonged to non-Gaussian distribution populations which limited the analysis to non-parametric methods. The Wilcoxon two-tailed rank sum test validated the hypothesis to 95% confidence that the descriptors from Reagent Set A and those from Reagent Set B are drawn from statistically different populations. The test also validated the hypothesis that the descriptors from replicate runs of Reagent Set A are drawn from statistically similar populations. Thus, the statistical methods were able to distinguish between signals due to noise/background and those due to reaction activity.

Principal components analysis of the multidimensional descriptor data did not uncover an underlying structure of the data.

K-means clustering of the multidimensional descriptor data, followed by analysis of the averaged power spectrums was ineffective.
Chapter Three - Iodate Studies

"Attention to detail is essential for gleaning information from an unsuspecting source."

- Insp. Clouseau

3.1 Introduction

The preliminary studies documented in Chapter Two described a system which moved the reagents into the reaction cell manually via 25.00 mL pipettes and pipette bulbs. While practical, simple, and cost-effective, this type of delivery system is slow, lacks mixing repeatability and is prone to operator error. Since one of the goals of this work was to study the Briggs-Rauscher iodine clock over a range of chemical and physical conditions, an improved delivery system was required.

This chapter documents the next step in the evolution of the experimental system from Chapter Two. Reagent delivery is automated using components of the FIDO system (see Glossary). The detection system is also improved by supplementing the CAE detector with an ion-selective electrode (ISE) and an ultra-violet/visible diode-array spectrophotometer (UV-Vis).

Obtaining the same performance from an ISE in a flow system as in a manual system poses some challenges. While some researchers have reported significant gains in sensitivity\textsuperscript{44}, this is usually at the expense of peak broadening and incomplete baseline
A more serious problem is the appearance of “overshoot” peaks, first observed by Linder under steady-state conditions. These peaks have been attributed to sudden changes in activity at the electrode surface as a result of the desorption of primary ions due to the adsorption of excess interferent ions. In later work, Linder reported that no overshoots were observed when a chloride-selective electrode was used to monitor iodide ions. Based on this work, we decided to employ a chloride-selective electrode for our studies.

The Briggs-Rauscher (BR) oscillator has been extensively studied via UV-Vis spectrophotometry. UV-Vis provides a rapid and repeatable analysis which is widely used in flow systems. Many of the species in the BR oscillator absorb in the UV-Vis region giving the researcher a choice of wavelengths to monitor. Table 3-1 lists some of the species and their extinction coefficients where known. In this work, we are primarily interested in the aqueous iodine peak at 460nm.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Species</th>
<th>Formula</th>
<th>$\varepsilon$ (M$^{-1}$cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>iodomalate</td>
<td>ICH(COOH)$_2$</td>
<td>209</td>
<td>48</td>
</tr>
<tr>
<td>310</td>
<td>hypoiodous acid</td>
<td>HOI</td>
<td>200</td>
<td>49</td>
</tr>
<tr>
<td>352</td>
<td>tri-iodide ion</td>
<td>I$_3^-$</td>
<td>26400</td>
<td>50</td>
</tr>
<tr>
<td>460</td>
<td>aqueous iodine</td>
<td>I$_2$(aq)</td>
<td>746</td>
<td>50</td>
</tr>
</tbody>
</table>
3.2 Experimental

3.2.1 Briggs-Rauscher Chemical System

One set of stock reagents was used for these studies. The commercially available chemicals were used without further purification. The maximum concentrations of each stock reagent can be found in Table 3-2. The ionic strength adjuster (ISA) was prepared as 5 M NaNO₃. The hydrogen peroxide concentration was determined twice daily using titanium(IV) oxalate and the starch solution was prepared fresh each day by vigorously boiling the requisite amount of starch in distilled water until the originally clear solution turned translucent, both as mentioned in Chapter Two.

Table 3-2. Reagents used for batch studies.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Source and Grade</th>
<th>Maximum Reagent Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>BDH, ACS Analytical</td>
<td>0.8500 M</td>
</tr>
<tr>
<td>KIO₃</td>
<td>BDH, ACS Analytical</td>
<td>0.0375 M</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>BDH, ACS Analytical</td>
<td>0.0401 M</td>
</tr>
<tr>
<td>CH₂(COOH)₂</td>
<td>Fisher, ACS</td>
<td>0.0370 M</td>
</tr>
<tr>
<td>MnSO₄</td>
<td>MacArthur, ACS</td>
<td>0.0201 M</td>
</tr>
<tr>
<td>ISA</td>
<td>Orion, ACS</td>
<td>0.2% v/v</td>
</tr>
<tr>
<td>starch</td>
<td>BDH, ACS Analytical</td>
<td>0.13% v/v</td>
</tr>
</tbody>
</table>
3.2.2 Instrumental System

The instrumental apparatus is illustrated in Figure 3-1; single lines represent the flow of data and/or control signals in the direction of the arrows, while the larger lines with hatchings represent the flow of reagents or the reaction mixture. A brief summary of each component's make, model and settings are given in Table 3-3. Information about the manufacturers can be found in Appendix A. Selected components are described in more detail in the following subsections.

Figure 3-1. Apparatus for iodate studies. The acronyms are defined in Glossary.
Table 3-3. Apparatus list for iodate studies.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Instrument Description</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Settings/Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMP</td>
<td>conditioning amplifier</td>
<td>Brüel &amp; Kjær</td>
<td>2638</td>
<td>40 dB gain</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100 - 2000 kHz filter</td>
</tr>
<tr>
<td>CTB</td>
<td>constant temp. bath</td>
<td>Blue M Electric</td>
<td>M-W</td>
<td>varied by experiment</td>
</tr>
<tr>
<td>DACA</td>
<td>a/d and d/a converter</td>
<td>IBM</td>
<td>DACA</td>
<td>varied by experiment</td>
</tr>
<tr>
<td>FIDO</td>
<td>see Glossary</td>
<td>in-house</td>
<td>n/a</td>
<td>varied by experiment</td>
</tr>
<tr>
<td>HPIB</td>
<td>see Glossary</td>
<td>Hewlett-Packard</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>ISE</td>
<td>ion selective electrode</td>
<td>Orion</td>
<td>94-17B</td>
<td></td>
</tr>
<tr>
<td>P-PC</td>
<td>primary computer</td>
<td>Nora Systems</td>
<td>286/12</td>
<td></td>
</tr>
<tr>
<td>PCIP</td>
<td>pc adapter oscilloscope</td>
<td>MetraByte</td>
<td>PCIP</td>
<td>8 mV resolution</td>
</tr>
<tr>
<td></td>
<td>card</td>
<td></td>
<td></td>
<td>2.50 MHz samp.freq.</td>
</tr>
<tr>
<td>PT</td>
<td>broad-band piezoelectric</td>
<td>Brüel &amp; Kjær</td>
<td>8312</td>
<td>40 dB gain</td>
</tr>
<tr>
<td></td>
<td>transducer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RS-232</td>
<td>serial port interface</td>
<td>see below</td>
<td>n/a</td>
<td></td>
</tr>
<tr>
<td>S-PC</td>
<td>secondary computer</td>
<td>Campus Computers</td>
<td>386/20</td>
<td></td>
</tr>
<tr>
<td>UV-VIS</td>
<td>spectrophotometer</td>
<td>Hewlett Packard</td>
<td>8452A</td>
<td>varied by experiment</td>
</tr>
<tr>
<td></td>
<td>w/ 1 cm path length</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>quartz flow cell</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.2.1 Constant Temperature Bath

The stock reagents were poured into 250 mL Erlenmeyer flasks, covered with Parafilm®, and placed inside the constant temperature bath. A small hole was punched through each Parafilm® seal to allow the insertion of Teflon (PTFE) tubing. A mixture of
50% v/v MeOH/water was also placed in the bath in a similar manner, to be used as a cleaning solution between experimental runs.

An electronic temperature monitor was attached to the bath and its output connected to the primary computer via the DACA interface. The computer could then monitor and record the bath's temperature as the experiments progressed.

3.2.2.2 Flow Injection Development and Optimization System (FIDO)

This instrumentation housed the peristaltic pumps and gas-actuated valves which were used to deliver the reagents to the reaction vessel. The system has undergone substantial development and improvement since its first construction. Details of the interface circuitry can be found elsewhere. New software, written by this author to operate the system, is described in Appendix B. A schematic diagram of the flow system is illustrated in Figure 3-2. A list of components is in Table 3-4. On the left of the figure is the constant temperature bath. The flow system is represented as the collection of pumps (Pn) and valves (Vn). The funnel is the reaction vessel and UV-VIS is the UV-Visible spectrophotometer. Unlike the previous figure, only reagent flow is indicated, there are no control or data lines shown.
Table 3-4. Flow system components.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P1-P5)</td>
<td>Peristaltic pump</td>
<td>Ismatec</td>
<td>2/6</td>
<td>0-76 rpm in 256 steps</td>
</tr>
<tr>
<td>(P6)</td>
<td>Peristaltic pump</td>
<td>Alitea</td>
<td>C4V</td>
<td>0-125 rpm in 4096 steps</td>
</tr>
<tr>
<td>(V1-V2)</td>
<td>Gas-actuated valve</td>
<td>Rheodyne</td>
<td>type 50</td>
<td>six port</td>
</tr>
</tbody>
</table>

The five vertical peristaltic pumps drew reagents from their containers in the constant temperature bath to the reaction vessel at a rate of ca. 5 mL/min. Tygon® pump tubing, 1.52 mm I.D., was used for all pumps except the pump interfaced to the methanol/water line. This pump required Viton® pump tubing (also 1.52 mm I.D.) which
is solvent resistant. (aside: two forms of tubing are normally used in a flow analysis project of this nature. The first, Teflon® (PTFE) tubing, is the tubing used to deliver the reagents to and from the pump. In this work, insulated 0.8 mm I.D. tubing was used. The second form, poly(vinylchloride) (PVC) pump tubing, is used with the pumps themselves. The rollers on the pump alternately pinch the tubing, and roll to propel the desired solution. The PTFE tubing should fit snugly inside the pump tubing.) Note that while the tubing in the figure is drawn as different lengths, in fact all the tubing was carefully cut to the same length (ca. 200 mm), ensuring that the necessary quantities of reagent arrived at the reaction vessel nearly simultaneously.

Prior to an experimental run, the pumping rate of pumps P1 - P6 were calibrated utilizing a simple gravimetric procedure where a known amount of distilled water is pumped during a known period of time at a fixed RPM, and the weight difference measured.

During an experiment the reagents were delivered simultaneously to the reaction vessel at a rate of ca. 5 mL/min via pumps P1 to P5. The total initial reaction volume was 10.0 mL. Once all reagents had been delivered, the flow system activated pump P6 to begin cycling the reaction mixture through the UV-Vis detector. With valve V2 in the “cycle” position, the reaction mixture was returned to the reaction vessel. This constant cycling at a rate of ca. 8.5 mL/min provided adequate mixing and a mean residence time of ca. 120 seconds. With valve V2 in the “waste” position, the reaction mixture was sent to the waste container.
3.2.2.3 Reaction Vessel

The reaction vessel is illustrated in Figure 3-3. The compact design precludes the use of a mechanical stirrer; all mixing was provided by the cycling mentioned above. In this way, any possible reactions which might have occurred on the stirrer’s metal surface are avoided.

The reaction vessel consisted of a short-stemmed Pyrex® funnel with an internal diameter of 50 mm at its widest point, an internal diameter of 5 mm at the stem, a stem length of 25 mm, and an overall length of 60 mm. The funnel’s stem was pushed through a rubber stopper which in turn was fastened to a retort stand via a standard clamp (not shown for clarity). The rubber stopper provided limited insulation against benchtop vibration.

A piezoelectric transducer was affixed to one side of the funnel (through a thin layer of acoustic couplant grease) with black electrical tape. The tape was wrapped around both the transducer and the funnel in several layers to provide adequate thermal insulation and protection from ambient light.

![Diagram of reaction vessel](Image)

Figure 3-3. The reaction vessel in detail.
3.2.2.4 Ion Selective Electrode (ISE)

The iodide potential in solution was measured via an ISE mounted such that the electrode’s sensing surface was completely immersed in the reaction mixture. The ISE used was rated to be sensitive to iodide over a range of $1 \text{ M}$ to $5 \times 10^{-6} \text{ M}$, and boasted an internal reference electrode which obviated the need for an external one. Twice each day, the electrode operation was tested against iodide standards and the resulting slope of the calibration curve checked against the manufacturer’s specifications. Before each experiment, the sensing element required polishing to remove any build-up of hypohalous salts on the membrane’s surface. Following that, an $E^0$ value was obtained by immersing the electrode in a solution containing all reagents except the iodate.

3.2.2.5 Primary Computer

The primary computer exerted control over and collected data from the various instruments via three different interfaces. The data acquisition and control adapter (DACA) was used to control the flow system, to collect data from the temperature sensor in the constant temperature bath, the ion selective electrode, and the transducer (via the amplifier’s d.c. rms output). The HPIB interface provided control over the UV-Vis spectrophotometer. The RS-232 port, through a null-modem cable, allowed the primary computer to communicate with the secondary computer.

3.2.2.6 Secondary Computer

The secondary computer’s single task was to collect CAE signals from the transducer via the amplifier’s a.c. output. The acquisition and storage of CAE signals proved to be too demanding to be included with the other devices, which is why a dedicated computer was necessary. As mentioned above, the RS-232 port provided
communication and synchronization between the two computers. This work is the first time the flow analysis system had been used with two computers. Significant software development by this author was necessary to complete the system.

3.2.3 Methods

The immediate goal was to collect information from three separate detectors over a range of reagent concentrations and temperatures. The result was a three dimensional grid with the axes reaction temperature, reagent, and concentration, measured as a function of time.

3.2.3.1 Reaction Temperature

Since the BR oscillator operates well under room temperature conditions, we selected a series of temperatures close to room temperature: 20, 25, 30 and 35 degrees Celsius.

3.2.3.2 Reagents and Concentrations

Ideally, we would like to systematically vary all the reagents which make up the BR oscillator, but time and equipment constraints limit the scope of our investigations. Initially we decided to explore the role of iodate in the oscillator by varying the [iodate] from 0.0038 to 0.0375 M. A series of hydrogen peroxide experiments were also conducted, but only at one temperature: 35°C. The [H₂O₂] was varied from 0.0850 to 0.8500 M. The H₂O₂ work is covered in Chapter Four.

Each concentration region was explored in a series of ten steps, from low to high concentration. While one reagent was being varied, all others remained unchanged.
Constant reaction volume was maintained by the automated addition of distilled water. Table 3-5 outlines the experiments conducted. Since each series varies the concentration of a single reagent in ten steps, the table represents a total of 50 experiments.

Note that series PF-G is an exception. This series was intended as a trial run to test that the hardware and software was functioning correctly. However, the results from this run proved interesting and it was decided to include the findings in this discussion.

Table 3-5. Experimental Series.

<table>
<thead>
<tr>
<th>Series Name</th>
<th>Temp (°C)</th>
<th>Reagent Varied</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-G</td>
<td>20</td>
<td>iodate</td>
</tr>
<tr>
<td>PF-K</td>
<td>25</td>
<td>iodate</td>
</tr>
<tr>
<td>PF-O</td>
<td>30</td>
<td>iodate</td>
</tr>
<tr>
<td>PF-T</td>
<td>35</td>
<td>iodate</td>
</tr>
</tbody>
</table>
3.3 Series PF-G, Iodate varied from 0.005 to 0.050 M, 20°C

This series was designed to test that all the equipment and software was functioning acceptably. The concentrations of the reagents used in this series are listed here:

H₂SO₄  0.054 M  
Mn(II)  0.020 M  
CH₂(COOH)₂  0.050 M  
H₂O₂  1.24 M  
KIO₃  0.005 to 0.050 M  (in ten steps)

The instrument settings are shown in Table 3-6. All instruments except the oscilloscope were operated in a continuous mode which means the instruments collected a data point at the end of every sampling period. The scope, however, was operated in a triggered mode which means that the scope captured a CAE signal every time a preset trigger level was breached. See the section Timing and Methods in Chapter Two. In this work with the PCIP oscilloscope adapter card, a minimum of 1.5 seconds was required to capture and store a CAE signal.
3.3.1 Data Work-up

The raw data collected from the various instruments required some preprocessing before an analysis could be conducted.

- **CAE d.c.** - the digitized signal was corrected for amplification and then the background level was subtracted (30 seconds of background level was captured before every experimental run).

- **ISE** - the data from the ion-selective electrode were initially corrected for amplification, the value of $E^o$ subtracted, and then the [iodide] assigned based on calibration curves. The electrode was calibrated at the start of every experimental series.

- **UV-Vis** - the data from the UV-Vis spectrophotometer were automatically blank-subtracted by the UV-Vis itself before transmission to the primary computer (a blank was taken before every experiment). The concentration of aqueous iodine was calculated from the absorbance at 460 nm.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Samp. Period</th>
<th>Other settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE d.c.</td>
<td>4.0 s</td>
<td>64 dB gain</td>
</tr>
<tr>
<td>ISE</td>
<td>4.0 s</td>
<td>20x linear gain</td>
</tr>
<tr>
<td>scope</td>
<td>min. 1.5 s</td>
<td>1600 mV input range, 2.5 MHz digitization rate</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>4.0 s</td>
<td>300 to 600 nm; 2 nm resolution</td>
</tr>
</tbody>
</table>
3.3.2 PF-G-1 and 2

The data from PF-G-1 (initial [iodate] = 0.005 M) and 2 (initial [iodate] = 0.010 M) are presented in figure C-5. The first run shows no UV-Vis or ISE activity. There is some acoustic activity, but this may be due to line noise or to the side reaction involving the oxidation of malonic acid by Mn(III):

\[
\text{CH}_2(\text{COOH})_2 + 2\text{H}_2\text{O} + \text{Mn(III)} \rightarrow \text{HCOOH} + 2\text{CO}_2 + 6\text{H}^+ + \text{Mn(II)}
\]

This particular reaction has not been observed by other workers, but similar work has been done with Ce(IV)\textsuperscript{53}. Mn(III) can also oxidize organic compounds, but such experiments are difficult to do quantitatively\textsuperscript{54}.

An attempt was made to determine if the malonic acid oxidation was the primary acoustic source by directing any evolved gas into the sampling loop of a gas partitioner (Fisher-Hamilton, Model 29). This instrument is a gas chromatograph specifically designed for the quantitative determination of substances which are gaseous at room temperature. It employs a dual-column, dual-detector chromatographic system to separate and measure carbon dioxide, oxygen, nitrogen, methane, and carbon monoxide. Unfortunately, reproducible results could not be achieved and so conclusions cannot be drawn at this time.

The second run shows a slight increase in both the UV-Vis and the ISE trace, indicating the build-up of aqueous iodine and iodide ion, but not enough to commence oscillations. The CAE trace also shows a little more activity suggesting that an acoustically emissive chemical reaction is taking place with greater vigor.
3.3.3 PF-G-3 and 4

In PF-G-3 (initial \([\text{iodate}] = 0.015 \text{ M}, \) figure C-6) the ISE trace shows four distinct regions: an induction period of ca. 20 seconds, a reagent "build-up" phase of ca. 100 seconds, regular, small amplitude oscillations for ca. 220 seconds and finally a drop towards the baseline. Normally only three regions are expected: induction, oscillation and termination (recall the experiments in Chapter Two). The presence of four regions may be due to lack of rapid mixing. Cooke noted that in the absence of stirring, the behaviour of the BR oscillator is markedly dependent on the size of the reaction vessel. Specifically, Cooke observed that the amplitude of iodide ion oscillations decreased, then increased again as the reaction proceeded\(^5\). This may be due to variation in the amount of dissolved oxygen. If so, then the behaviour of the BR oscillator would be dictated by the availability of reaction vessel surface nucleation sites. The accompanying CAE would be dependent upon the available surface area of the gas/liquid interface to accommodate bubble bursting. It is with these considerations in mind that a funnel-shaped reaction vessel was chosen which affords large surface areas for both bubble nucleation and bubble bursting while simultaneously providing sufficient depth to allow the submersion of the ISE.

The small size of the reaction vessel prohibits the use of stirring devices. Instead, mixing is provided by continuously drawing the reaction mixture from the bottom of the reaction vessel, through the UV-Vis, and back into the top of the reaction vessel via a pump which circulates the reaction mixture at a rate of ca. 8.5 mL/min. This system is not perfect, but provides better results than a solely diffusion-controlled system.

The UV-Vis trace corroborates the ISE trace. An added feature is the steady positive slope indicating a build-up of aqueous iodine. The data with the induction period
removed, was plotted LN([iodine]) and 1/[iodine] vs time, and are depicted in Figure 3-4. A linear regression was performed on each plot. The correlation coefficients for the three LN(iodine) plots are presented. It is apparent that the rate does not follow a strictly first or second order trend.
Figure 3-4. Plots of LN([iodine]) and 1/[iodine] vs. Time for runs PG-G-2, PF-G-3 and PF-G-4. In all cases the induction period data has been removed.
The CAE trace for PF-G-3 (Figure C-6) shows sporadic oscillations while that for PF-G-4 shows almost regular oscillations of varying amplitudes. Of interest here is the apparent lack of an induction period. Recall from Chapter Two that a significant induction period was observed in all the experiments discussed. Also note that both the ISE and UV-Vis traces suggest an induction period is occurring. This discrepancy merits further investigation.

The ISE data from the four runs discussed above indicate that under these conditions, oscillations occur when the initial iodate concentration is greater than 0.010 M (PF-G-3). The UV-Vis data are inconclusive on that point. The CAE d.c. does not show significant activity until PF-G-4 ([iodate]=0.020 M) which is in keeping with the work of Roux and Vidal which found the minimum iodate required for oscillations to be 0.019 M (under similar conditions).

The plot of [iodine] vs. time for PF-G-2, and to some extent PF-G-3, appears to show some periodicity, implying the presence of low frequency oscillations. Fourier transforms of these data sets showed no low frequency peaks and the autocorrelograms (Figure 3-5) were also negative. The apparent oscillations cannot be explained at this time.
Figure 3-5. Autocorrelograms of UV-Vis data for series PF-G-2, 3 and 4
3.3.4 PF-G-5 through 10

The initial iodate concentrations studied are G-5 (0.025 M), G-6 (0.030 M), G-7 (0.035 M), G-8 (0.040 M), G-9 (0.045 M), and G-10 (0.050 M).

In these runs, the BR reaction is seen to oscillate strongly. This provides peak data from which reaction rates can be calculated and plausible mechanisms introduced. Thus the data from these runs are analyzed a little more rigorously than for the previous runs.

3.3.4.1 Peak Count and Frequency

The data from runs 5 through 10 are shown in the figures C-7 through C-9. The UV-Vis trace (at 460 nm) takes on a skewed sawtooth appearance implying that the iodine production rates are faster than the iodine consumption rates. The ISE trace has a similar sawtooth waveshape while the CAE traces have a variety of waveshapes. Several trends are more easily seen when peak data are compiled into a table, as in Table 3-7. Peak data were not included from the UV-Vis because reliable data could not be collected beyond PF-G-7 due to saturation of the detector. A shorter path length flow cell was not available to compensate for this.

For the purposes of this work, a peak visible in the data trace is considered synonymous to an oscillation and is defined as having an initial rise (positive slope) of at least 12 seconds duration, a peak of not more than four seconds duration, followed by a drop (negative slope) of at least 12 seconds duration. This definition is not entirely arbitrary: the data were sampled at a rate of 0.25 Hz, thus each slope is guaranteed a minimum of three data points. Hence, each peak is defined by a minimum of ten data points.
Table 3-7. Peak parameters for Series PF-G.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>CAE DC Number of peaks</th>
<th>CAE DC Number of peaks/min.</th>
<th>ISE Number of peaks</th>
<th>ISE Number of peaks/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-G-5</td>
<td>0.020 M</td>
<td>8</td>
<td>1.60</td>
<td>13</td>
<td>2.60</td>
</tr>
<tr>
<td>PF-G-6</td>
<td>0.025 M</td>
<td>11</td>
<td>2.20</td>
<td>13</td>
<td>2.60</td>
</tr>
<tr>
<td>PF-G-7</td>
<td>0.030 M</td>
<td>12</td>
<td>2.40</td>
<td>12</td>
<td>2.40</td>
</tr>
<tr>
<td>PF-G-8</td>
<td>0.035 M</td>
<td>12</td>
<td>2.40</td>
<td>13</td>
<td>2.60</td>
</tr>
<tr>
<td>PF-G-9</td>
<td>0.040 M</td>
<td>10</td>
<td>2.00</td>
<td>10</td>
<td>2.00</td>
</tr>
<tr>
<td>PF-G-10</td>
<td>0.045 M</td>
<td>11</td>
<td>2.20</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

The “number of peaks” column in the table refers to the number of peaks between 100 and 400 seconds. This range was chosen to help eliminate interference from either the induction or termination phases. The CAE d.c. data show that as the initial [iodate] increases, the number of peaks increases until a maximum is reached at PF-G-7. Then the number of peaks begins to decrease as [iodate] increases. The number of iodide peaks, however, remains generally constant with increasing [iodate] until PF-G-9. The exception to these observations is PF-G-10, which had the strongest initial concentration of iodate. In this run, the iodide concentration remained low for ca. eight minutes before increasing beyond the capacity of the ISE to measure. Such behaviour typically occurs when the
ISE's membrane has become contaminated with I₂ precipitate. There was also an adverse effect on the CAE which posted low peak numbers and frequency.

These differences may be explained by examining the kinetics of the peak slopes. Cooke\textsuperscript{55} reported that iodine production was enhanced by an increased iodate concentration while iodine consumption remained nearly constant. To test this observation against our data, the slopes of all the peaks were measured and then averaged. The results are shown in Table 3-8. Recall the terminology introduced in Chapter Two where a Neg phase referred to the part of the peak where \(d(\text{response})/dt\) has a negative slope and a Pos phase a positive slope. In the case of the ISE (monitoring iodide ion), a Pos phase represents production of iodide ion and a Neg phase is consumption of iodide ion. For the UV-Vis data (monitoring iodine), a Pos phase represents production of iodine and Neg phase consumption of iodine. In Chapter Two it was suggested that the primary source of CAE in the BR reaction is oxygen evolution, in which case the phases represent increasing and decreasing gas evolution, respectively.
Table 3-8. Reaction rates for Pos and Neg events for series PF-G.

<table>
<thead>
<tr>
<th>Run</th>
<th>CAE Pos (x10³ mV·s⁻¹)</th>
<th>CAE Neg (x10³ mV·s⁻¹)</th>
<th>[iodide] Pos (x10⁰ M·s⁻¹)</th>
<th>[iodide] Neg (x10⁰ M·s⁻¹)</th>
<th>[iodine] Pos (x10² M·s⁻¹)</th>
<th>[iodine] Neg (x10² M·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.20±0.48</td>
<td>-5.20±0.51</td>
<td>9.98±0.20</td>
<td>-8.93±0.32</td>
<td>29.2±4.2</td>
<td>-24.1±2.7</td>
</tr>
<tr>
<td>6</td>
<td>6.10±0.40</td>
<td>-6.74±0.28</td>
<td>11.4±0.41</td>
<td>-8.12±0.39</td>
<td>34.3±2.3</td>
<td>-47.4±3.5</td>
</tr>
<tr>
<td>7</td>
<td>8.96±0.44</td>
<td>-8.19±0.54</td>
<td>14.5±0.51</td>
<td>-9.61±0.25</td>
<td>46.6±2.0</td>
<td>-57.5±2.5</td>
</tr>
<tr>
<td>8</td>
<td>8.94±0.40</td>
<td>-8.23±0.43</td>
<td>16.5±0.52</td>
<td>-14.9±0.44</td>
<td>75.0±3.8</td>
<td>-61.9±3.0</td>
</tr>
<tr>
<td>9</td>
<td>10.2±0.72</td>
<td>-9.43±0.61</td>
<td>14.1±0.49</td>
<td>-7.54±0.38</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>11.6±0.75</td>
<td>-9.11±0.59</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

3.3.4.2 Peak Reaction Rates

The data in the table for all three analytical methods show a steady increase in reaction rate with increasing run number (hence increasing initial [iodate]), for both Pos and Neg phases, the only exception being the ISE data for PF-G-9 and the CAE data for PF-G-10 (already noted above). A graphical depiction (Figure 3-6) of the data provides interesting results. In agreement with Cooke’s observations, the iodine production rates show the beginning of an almost exponential growth, while the iodine consumption rates decrease at an almost exponential rate. The CAE Pos rate is nearly linear (r² = 0.914) and closely parallels the iodide ion production rate (r² = 0.982). The CAE Neg rate is also linear (r² = 0.935) but the iodide ion consumption rate rapidly deviates from linearity for initial [iodate] = 0.035 M.
3.3.4.3 Phase Relationships

Phase relationships play a vital role in understanding the BR oscillator. They are difficult to see, however, unless the reaction is oscillating strongly. Figure 3-7 shows the phase relationships for the strongly oscillating system present in PF-G-7. As iodine falls to its minimum concentration, iodide ion increases to its maximum concentration. This
relationship has been noted by other workers\textsuperscript{57}. The CAE appears to parallel the production and consumption of iodine. This was an unexpected result, however, as oxygen is evolved primarily during iodide ion formation:

\[
\text{I2. } \text{HOIO} + I^- + H^+ \rightarrow 2\text{HOI}
\]
\[
\text{D1. } \text{HOI} + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O
\]
\[
\text{I1. } \text{HOI} + I^- + H^+ \leftrightarrow I_2 + H_2O
\]

Reaction D1 is the rate-limiting step in this sequence, and hence it is expected that iodine production would be significantly out of phase with oxygen evolution. The phase relationship which was observed may be explained by drawing conclusions from the work of Wentzell et al\textsuperscript{58}. In that work, it was suggested that oxygen produced from dissolved hydrogen peroxide is depleted through a diffusion pathway to atmosphere before bubble nucleation is energetically favoured. If the same model can be applied to this work, then a time delay would be expected from the time reaction D1 commences to the time at which bubble nucleation occurs (and hence acoustic activity is detected). This delay would alter the phase of the CAE, and might make it appear that CAE is in phase with iodine instead of with iodide ion.

Rubin and Noyes studied homogeneous nucleation of bubbles resulting from supersaturated solutions\textsuperscript{59}. They found there existed a threshold for nucleation beyond which it was impossible to push the level of supersaturation. Thresholds for diatomic gases such as O\textsubscript{2} all fell between 0.012 and 0.07 M, while that for CO\textsubscript{2} was 0.4 M. They also noted that temperature had little effect on the threshold.
3.3.4.4 Extent of Reaction

Recall from the Introduction in Chapter One, that an acoustic emission wave is a transient, elastic wave generated by a rapid mass motion of a collection of atoms. Thus every CAE “burst” represents a physicochemical event. If those bursts are integrated over time, the resulting curve represents the amount of chemical acoustic emission produced. Figure 3-8 shows the integrated CAE d.c. curves (top) and the integrated CAE d.c. at time = 600 seconds as a function of initial iodate concentration (bottom).

The data for PF-G-1 through PF-G-3 fit to a zero order function indicating that the rate of CAE is independent of the concentrations of the species involved. PF-G-4 (initial [iodate] = 0.020 M) through PF-G-9 fit well to a first order rate law. Note the common
Table 3-9. Curve fit results of integrated CAE d.c. data.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>( r^2 )</th>
<th>see</th>
<th>( k ) (( \times 10^3 ) s(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-G-4</td>
<td>0.020 M</td>
<td>0.999</td>
<td>0.202</td>
<td>1.21</td>
</tr>
<tr>
<td>PF-G-5</td>
<td>0.025 M</td>
<td>0.998</td>
<td>0.320</td>
<td>2.69</td>
</tr>
<tr>
<td>PF-G-6</td>
<td>0.030 M</td>
<td>0.998</td>
<td>0.364</td>
<td>2.42</td>
</tr>
<tr>
<td>PF-G-7</td>
<td>0.035 M</td>
<td>0.998</td>
<td>0.535</td>
<td>1.13</td>
</tr>
<tr>
<td>PF-G-8</td>
<td>0.040 M</td>
<td>0.996</td>
<td>0.840</td>
<td>1.17</td>
</tr>
<tr>
<td>PF-G-9</td>
<td>0.045 M</td>
<td>0.997</td>
<td>0.971</td>
<td>1.22</td>
</tr>
</tbody>
</table>

induction period of ca. 25 seconds, which was not apparent in the peak data, but is in evidence in this graph as a linear portion of the curve.

The rates in the above table show an interesting trend. There is a steady increase which reaches a maximum at PF-G-5, suddenly plummets, then begins to rise again. Note from Table 3-8 (page 84) that all three analytical methods reported similar rates for their pos and neg phases, suggesting that the oscillator is working at peak efficiency. A reasonable conclusion is that for the concentration range studied, and at the concentrations of the other components used, an initial [iodate]=0.025 M is optimum for oscillations to occur.

The data in the lower graph produces a straight line when plotted as in Figure 3-9. The total integrated CAE decreases with increasing initial [iodate] at a rate of -35.0 M\(^{-1}\). This is in agreement with Cooke\(^{30}\) who reported that cessation of the oscillations leading to iodine precipitation was favoured by an increase in iodate concentration. This is because high concentrations of iodate favour iodine production over iodine consumption.
(via iodination of malonic acid). These results also support the hypothesis that the source of chemical acoustic emission in the BR oscillator is bubble nucleation rather than iodine precipitation, or else we would see increased integrated CAE as initial [iodate] increases.
Figure 3-8. Top: integrated CAE d.c. signal vs. reaction time. The numbers beside each curve identify the experimental run. Bottom: Integrated CAE d.c. (at time = 600 sec) vs. initial iodate concentration.
Integrated CAE Study

Figure 3-9. Plot of LN(integrated CAE d.c.) vs. initial iodate concentration.

$r^2 = 0.996$
rate = -35.04 M$^{-1}$
3.3.5 Series PF-G: Conclusions

The data shown in figure 3-9 illustrate the quantitative analytical potential of chemical acoustic emission. The agreement was better than expected.

The ISE’s membrane surface required careful polishing with emery cloth at the beginning of every experimental run to remove build-up of AgI on the surface. The UV-Vis detector saturated before the end of the experiments. The next section will detail the improvements to the experimental system to overcome these limitations.

The experimental runs in which regular oscillations were not evident (runs PF-G-1 through 3), provided kinetic information about the reduction of iodate to iodine in the presence of hydrogen peroxide. The rate of iodine production was found to obey a first order rate law.

The data from the ISE suggest that the minimum concentration of iodate required to commence oscillations is 0.015 M. The CAE data does not concur, and instead supports the claim of Roux and Vidal\textsuperscript{56} that a minimum of 0.019 M is required.

The reaction rates of the Pos and Neg phases indicated that the rate of iodine production increases with increased iodate while the rate of consumption increases only slightly, which confirms Cooke’s observations\textsuperscript{30}. The CAE’s Pos rate was found to closely parallel the iodide ion’s production rate, but the CAE’s Neg rate paralleled the iodide ion’s consumption rate only at low iodate concentrations. At high iodate concentrations, the iodide ion consumption rate increases dramatically.

Even though reaction rates for the CAE parallel those for the iodide ion, the phase relationships showed that CAE parallels that for iodine, not iodide ion.
Finally, the case of the missing CAE induction period was solved. While not easily visible in the raw CAE traces, an induction period of ca. 25 seconds is apparent from the CAE cumulative sum graph (Figure 3-8 on page 90). The experiments in which a reaction was not seen to take place (PF-G-1 through 3) resulted in a linear function of the integrated CAE d.c. The remaining series PF-G-4 through PF-G-9 fit well to a first order function. The integrated CAE d.c. at time = 600 seconds as a function of initial [iodate] was found to decrease at a rate of 35.0 M$^{-1}$ indicating that CAE is in the BR oscillator due to bubble nucleation rather than precipitation.
Series PF-G provided useful information about the chemical system as well as the instrumental system. It demonstrated that an ISE was not easily adapted to an automated flow system and that the UV-Vis reached saturation conditions before the entire series could be completed.

Series PF-K is the first of the “formal” iodate series, and hence the first series to use a slightly modified experimental system. The changes are as follows:

1. The ISE was no longer in use. The need to polish the ISE’s membrane before every experimental run negated one of the advantages of an automated system: the ability to operate unattended. Hence it was decided to take the ISE out of the loop and to continue using the CAE and the UV-Vis detectors. Another concern was the potential poisoning of the ISE. Sandifer exposed a chloride ISE to bromide and found that prolonged exposure led to the formation of AgCl\textsubscript{x}Br\textsubscript{y} crystals throughout the membrane, not just at the surface\textsuperscript{60}. However, no gross deterioration of ISE response had been detected in the present work.

2. The sampling period was decreased from 4.0 to 3.0 seconds to increase the resolution of the spectra. Because limited data space was available, the total acquisition time was decreased to 480 seconds from 600. We felt that this would still provide a safe margin as the PF-G experiments indicated that oscillations generally terminated before 420 seconds.

3. Initial concentrations of key species were reduced by approximately 25% to avoid UV-Vis detector saturation. See Table 3-2 above for the complete list of reagents and their concentrations.
3.4.1 Data Work-up

The raw data collected from the various instruments required some preprocessing before an analysis could be conducted. The work-up is identical to that described for the previous series.

Table 3-10. Instrument parameters for series PF-K.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Samp. Period</th>
<th>Other settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE d.c.</td>
<td>3.0 s</td>
<td>64 dB gain</td>
</tr>
<tr>
<td>scope</td>
<td>min. 1.5 s</td>
<td>1600 mV input range, 2.5 MHz digitization rate</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>3.0 s</td>
<td>300 to 600 nm; 2 nm resolution</td>
</tr>
</tbody>
</table>

3.4.2 PF-K-1 and 2

The data from PF-K-1 and 2 are presented in Figure C-10. PF-K-1 (initial [iodate] = 0.004 M) shows no UV-Vis activity other than the occasional bubble resulting in a sharp spike on the UV-Vis trace. There is some periodic acoustic activity.

The data for PF-K-1 shows an initial periodicity equal to 3\( \tau \), or 18 seconds. PF-K-2 shows the same periodicity. In the absence of visible oscillations, this long-period periodicity is likely due to the catalytic decomposition of hydrogen peroxide which has a net stoichiometry of:

\[
\text{Eqn 3-1.} \quad 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]
If the model proposed by Wentzell (discussed in the last section) is accurate, then bubble formation occurs only when the dissolved oxygen process is energetically unfavourable, i.e. when the solvent has reached oxygen saturation. Hence, there will be a periodic “pressure release” in the form of bubble evolution which appears on the CAE trace as a low rise.

The second run, PF-K-2 (initial \([\text{iodate}] = 0.008 \text{ M}\) ), shows a slight increase in the UV-Vis after ca. 360 seconds, indicating a build-up of aqueous iodine, but not enough to commence oscillations. The CAE trace also shows a little more activity suggesting that an acoustically emissive process (as described above) is taking place with greater vigor.

### 3.4.3 PF-K-3 and 4

In PF-K-3 (initial \([\text{iodate}] = 0.011 \text{ M}\) ), the UV-Vis trace shows a lot of activity, suggesting the possibility that the BR reaction is taking place. However, the irregular shape and distribution of the peaks indicates that the activity is due to extensive bubble evolution, rather than iodine absorption. Also, looking ahead to PF-K-4 (initial \([\text{iodate}] = 0.015 \text{ M}\) ), we see a mostly quiet trace which is expected for this level of iodate (cf. PF-G-3).

The regular oscillations in the previous CAE traces have become less regular in PF-K-3, but larger in amplitude suggesting that either the existing acoustically emissive process is being replaced by another CAE process or it is being supplemented by one. The autocorrellogram for PF-K-3 shows that the periodicity has increased to \(4\tau\), or 24 seconds, lending support to the hypothesis that a change is underway. The autocorrellogram for PF-K-4 shows almost random fluctuations and the results for PF-K-5 through 10 also yield no useful information and so are not included in this work. This suggests that as the \([\text{iodate}]\) increases to a level where oscillations become possible, the
catalytic decomposition of hydrogen peroxide is no longer the dominant method of oxygen evolution. This hypothesis is tested further in the sections to follow.
Figure 3-10. Autocorrelograms of CAE d.c. data for series PF-K-1 through 4. The time constant (τ) is six seconds.
3.4.4 PF-K-5 through 10

The initial iodate concentrations studied are K-5 (0.019 M), K-6 (0.023 M), K-7 (0.026 M), K-8 (0.030 M), K-9 (0.034 M), and K-10 (0.037 M).

3.4.4.1 Peak Count and Frequency

The data from runs 5 through 10 are shown in the following figures C-12 through C-14. The UV-Vis trace for PF-K-5 shows irregular peaks, which are likely due to a combination of the initial stages of the oscillator and bubbles in the light path. The remaining UV-Vis traces take on a skewed sawtooth appearance implying that the iodine production rates are faster than the iodine consumption rates. Indeed, the later experiments (cf. PF-K-8 and 9) show a pronounced change in the consumption rates. Several trends are more easily seen when peak data are compiled into a table, as in Table 3-11.
The data in Table 3-11 show some interesting trends, which are detailed in the following paragraphs. The exception appears to be PF-K-10 (initial [iodate] = 0.037 M) which shows a sharp decrease in the number of CAE d.c. peaks and a sharp increase in the number of UV-Vis peaks compared with PF-K-9. This cannot be adequately explained at this time.

The CAE d.c. data from PF-K-5 to PF-K-9 show that as the initial [iodate] increases, the number of peaks increases to a maximum at PF-K-6, then drops. The UV-Vis data for PF-K-5 to PF-K-9 shows a similar trend, with the exception that the maximum is reached at PF-K-7.

Interpretation of the UV-Vis results can be explained by the difference in iodine production and consumption rates. As mentioned in the discussion for series PF-G,

Table 3-11. Peak parameters for series PF-K.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>CAE DC Number of peaks</th>
<th>CAE DC Number of peaks/min.</th>
<th>UV-Vis Number of peaks</th>
<th>UV-Vis Number of peaks/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-K-5</td>
<td>0.019 M</td>
<td>10</td>
<td>2.00</td>
<td>14</td>
<td>2.80</td>
</tr>
<tr>
<td>PF-K-6</td>
<td>0.023 M</td>
<td>13</td>
<td>2.20</td>
<td>16</td>
<td>3.20</td>
</tr>
<tr>
<td>PF-K-7</td>
<td>0.026 M</td>
<td>8</td>
<td>1.60</td>
<td>17</td>
<td>3.40</td>
</tr>
<tr>
<td>PF-K-8</td>
<td>0.030 M</td>
<td>8</td>
<td>1.60</td>
<td>15</td>
<td>3.00</td>
</tr>
<tr>
<td>PF-K-9</td>
<td>0.034 M</td>
<td>11</td>
<td>2.60</td>
<td>12</td>
<td>2.40</td>
</tr>
<tr>
<td>PF-K-10</td>
<td>0.037 M</td>
<td>4</td>
<td>0.80</td>
<td>20</td>
<td>4.00</td>
</tr>
</tbody>
</table>
increasing the [iodate] tends to increase the iodine production rate greater than the consumption rate. Thus, we would expect the following situations:

**Low [iodate]: Production rate slightly larger than consumption rate**

In this situation, I$_2$ would be produced at a slightly greater rate than could be scavenged by the organic substrate. The peak shape should consist of a shallow rise to a peak followed by a sharp drop. Moderate oscillation periods are expected.

**Moderate [iodate]: Production rate nearly equal to consumption rate**

Here, the increased [iodate] increases both the production and consumption rates until they are nearly equal. Hence, we expect to have a large number of oscillations over a large oscillation period. The reaction proceeds until one of the reagents is depleted (usually the malonic acid). Symmetrical, needle-shaped peaks are expected to dominate.

**High [iodate]: Production rate much greater than consumption rate**

At this level of [iodate], the production rate has increased more quickly than the production rate, and highly skewed peaks occur. Short oscillation periods are expected and the reaction terminates with extensive iodine precipitation.

### 3.4.4.2 Peak Reaction Rates

The reaction rates for the *pos* and *neg* phases of the CAE d.c. and UV-Vis data are in Table 3-12. The UV-Vis data lends support to the above discussion where it can be seen that the iodine production and consumption rates are nearly equal for PF-K-7 (initial [iodate] = 0.026 M) which is also the experimental run with the most peaks. In the
previous series, PF-G-5 (initial $\text{iodate} = 0.025 \text{ M}$) also posted nearly identical iodine production and consumption rates.

The rates are plotted in Figure 3-11. The CAE d.c. $\text{pos}$ and $\text{neg}$ rates are nearly linear and closely parallel the iodine rates. The exception in both cases is PF-K-7 (initial $\text{iodate} = 0.026 \text{ M}$) which shows dramatically increased rates. This was also true for PF-G-5. This confirms the earlier suggestion that an $\text{iodate}$ of at least 0.025 M is optimum for maximum iodine production and consumption rates.

Figure 3-11. Reaction rates for different initial iodate concentrations.
Table 3-12. Reaction rates for Pos and Neg events.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>CAE Pos $(x10^3 \text{mV}.\text{s}^{-1})$</th>
<th>CAE Neg $(x10^3 \text{mV}.\text{s}^{-1})$</th>
<th>[iodine] Pos $(x10^2 \text{M}.\text{s}^{-1})$</th>
<th>[iodine] Neg $(x10^2 \text{M}.\text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-K-5</td>
<td>0.019 M</td>
<td>2.45±0.19</td>
<td>-2.51±0.19</td>
<td>4.11±0.35</td>
<td>-3.32±0.32</td>
</tr>
<tr>
<td>PF-K-6</td>
<td>0.023 M</td>
<td>3.41±0.18</td>
<td>-3.60±0.15</td>
<td>8.13±0.47</td>
<td>-7.64±0.52</td>
</tr>
<tr>
<td>PF-K-7</td>
<td>0.026 M</td>
<td>6.97±0.24</td>
<td>-7.04±0.34</td>
<td>12.7±0.7</td>
<td>-12.8±0.5</td>
</tr>
<tr>
<td>PF-K-8</td>
<td>0.030 M</td>
<td>6.84±0.41</td>
<td>-7.05±0.40</td>
<td>20.3±1.3</td>
<td>-15.3±1.0</td>
</tr>
<tr>
<td>PF-K-9</td>
<td>0.034 M</td>
<td>7.57±0.17</td>
<td>-7.26±0.27</td>
<td>23.8±1.3</td>
<td>-15.4±1.2</td>
</tr>
<tr>
<td>PF-K-10</td>
<td>0.037 M</td>
<td>2.64±0.29</td>
<td>-2.95±0.34</td>
<td>5.71±0.33</td>
<td>-5.92±0.31</td>
</tr>
</tbody>
</table>

3.4.4.3 Extent of Reaction

Figure 3-12 shows the integrated CAE d.c. curves (top) and the integrated CAE at time = 480 seconds as a function of initial iodate concentration (bottom).

The plots in the upper graph appear to show essentially linear (zero order) behaviour. In fact, the data in the plots 5 through 9 fit better to a first order function, although the scatter in the data prevents an unequivocal conclusion.

Recall that for series PF-G, the rate peaked at [iodate] = 0.025 M (PF-G-5). In this series, the rate peaks dramatically at 0.026 M before decreasing. This further strengthens the hypothesis that an initial [iodate] of ca. 0.025 M is optimum for oxygen evolution.
The lower graph in Figure 3-12 depicts the integrated CAE d.c. traces at time = 480 seconds vs. initial [iodate]. The first four points (PF-K-1 through 4) exhibit linear behaviour. The next five points (PF-K-5 through 9) fit nicely to a second order function of the general stoichiometry:

Eqn 3-2. \( A + 2B \rightarrow Z \)

The differential form of the rate law is:

Eqn 3-3. \( \frac{dx}{dt} = 2k(a_o - x) (a_o - 2x) \)

where \( k \) is the rate constant, \( a_o \) is the initial quantity and \( x \) the quantity at time \( t \). In terms of CAE, \( a_o \) would be the background noise and \( x \) the cumulative CAE response. Note that the rate law would also be valid for:

Eqn 3-4. \( A + B \rightarrow Z \)

provided that the initial concentrations of the two species were the same.

Recall from the discussion of series PF-G, that both of the main oxygen producing reactions in the BR oscillator are second order:

O2. \( 2\text{HOO}^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \)

D1. \( \text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{O}_2 + \text{H}^+ + \text{H}_2\text{O} \)

In series PF-G, the integrated CAE d.c. decreased as initial [iodate] increased. For this run, we see the integrated CAE d.c. exhibit a linear behaviour until initial [iodate] increases beyond 0.015 M. At that point, the integrated CAE d.c. increases dramatically. Plotting the natural logarithm of the last five data points against time failed to produce a
straight line. A test for a second order function also failed, indicating there is no simple rate law to describe the data.

Figure 3-12. *Top:* integrated CAE d.c. signal vs. reaction time. The numbers beside each curve identify the experimental run. *Bottom:* Integrated CAE d.c. (at time = 480 s.) vs. initial iodate concentration.
3.4.5 Series PF-K: Conclusions

The CAE d.c. data for PF-K-1 through 4 exhibited some periodic activity even though the UV-Vis data indicated no reaction taking place. Autocorrelograms of the data determined that periodicity was present with a time constant of 18 seconds. This period lengthened to 24 seconds as the [iodate] increased to 0.011 M. It was hypothesized the activity was due to the slow decomposition of hydrogen peroxide, according to the dissolved oxygen model proposed by Wentzell. The long-period oscillations would be the result of the gradual build-up of dissolved oxygen followed by its release as bubble nucleation. Consider the following postulated cycle:

1. $O_2$ produced by the catalytic decomposition of $H_2O_2$ is dissolved into solution. The saturation ratio $\sigma$ continues to increase ($\sigma$ is defined as the ratio of the current concentration to the equilibrium concentration of dissolved gas).

2. When the solution becomes supersaturated ($\sigma$ reaches a critical level), there is a spontaneous formation of bubbles accompanied by a decrease in free energy. Bubbles may form in the bulk of the solution and/or on the surface of the reaction vessel. The latter is usually easier (ie. occurs at lower values of $\sigma$) than the former mainly due to two main parameters: contact angle and nucleation site geometry as stated in the Introduction.

3. The bubbles then rise to the liquid/gas surface and burst where they are detected by CAE as the rise to a peak.

4. When enough oxygen has been released ($\sigma$ decreases past its critical level), the evolved $O_2$ once again dissolves into solution and the CAE peak declines.
Examination of the CAE d.c. peak data revealed that there was no direct, simple correlation with either iodine or iodide ion.

The PF-K reaction rate data for *pos* and *neg* phases agreed with that observed for series PF-G. The rates for the two phases were nearly identical when [iodate] approached 0.025 M, for all the analytical methods employed and both series posted the largest overall CAE d.c. rate for this concentration.

The integrated CAE d.c. data demonstrated a shallow linear trend until the initial [iodate] increased beyond 0.015 M at which time the slope increased dramatically.

There exists a relationship between initial [iodate] and integrated CAE which appears to be quantitatively useful for [iodate] > 0.020 M.
3.5 Series PF-O, iodate varied from 0.004 to 0.037 M, 30°C

This series is the second iodate series. It uses the same experimental procedures as PF-K, the only difference being a five degree rise in temperature. As a reminder, the instrumental parameters are present in the following table.

Table 3-13. Instrument parameters for series PF-O.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Samp. Period</th>
<th>Other settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE d.c.</td>
<td>3.0 s</td>
<td>64 dB gain</td>
</tr>
<tr>
<td>scope</td>
<td>min. 1.5 s</td>
<td>1600 mV input range, 2.5 MHz digitization rate</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>3.0 s</td>
<td>300 to 600 nm; 2 nm resolution</td>
</tr>
</tbody>
</table>

3.5.1 Data Work-up

The raw data collected from the various instruments required some preprocessing before an analysis could be conducted. The work-up is identical to that described for the previous series.
3.5.2 PF-O-1 and 2

The data from PF-O-1 and 2 are presented in Figure C-15. PF-O-1 (initial [iodate] = 0.004 M) shows no UV-Vis or acoustic activity.

The second run, PF-O-2 (initial [iodate] = 0.008 M), is mostly linear save for the occasional peak likely due to bubbles in the light path. The CAE trace shows a little more activity than for PF-O-1. Referring back to series PF-K, approximately the same number of peaks are present, but the peaks are larger in amplitude suggesting that temperature has a positive effect on the catalytic decomposition of hydrogen peroxide.

3.5.3 PF-O-3 and 4

In PF-O-3 (initial [iodate] = 0.011 M) and PF-O-4 (initial [iodate] = 0.015 M), show peaks of an irregular shape and distribution indicating extensive bubble evolution, rather than iodine absorption.

3.5.3.1 Autocorrelation

In series PF-K, there was evidence for some periodicity in the CAE d.c. data for the first four experimental runs. The results were an initial periodicity of 18 seconds, which lengthened to 24 seconds before commencement of oscillations.

The autocorrelograms for PF-O-1 through 4 are in Figure 3-13. Each graph shows an initial periodicity of ca. 5τ, or 20 seconds. This compares well with series PF-K,
which reported initial periodicities of ca. 18 seconds which lengthened to 24 seconds. The same discussion as to the processes involved should apply here.
3.5.4 PF-O-5 through 10

The initial iodate concentrations studied are O-5 (0.019 M), O-6 (0.023 M), O-7 (0.026 M), O-8 (0.030 M), O-9 (0.034 M), and O-10 (0.037 M).

3.5.4.1 Peak Count and Frequency

The data from runs 5 through 10 are shown in the C-17 through C-19. The UV-Vis trace for PF-O-5 shows irregular peaks, which are likely due to a combination of the initial stages of the oscillator and bubbles in the light path. The remaining UV-Vis traces take on a skewed sawtooth appearance implying that the iodine production rates are faster than the iodine consumption rates. Several trends are more easily seen when peak data are compiled into Table 3-14.

<table>
<thead>
<tr>
<th>Series</th>
<th>CAE DC Number of peaks</th>
<th>CAE DC Number of peaks/min.</th>
<th>UV-Vis Number of peaks</th>
<th>UV-Vis Number of peaks/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-O-5</td>
<td>3</td>
<td>0.60</td>
<td>14</td>
<td>2.80</td>
</tr>
<tr>
<td>PF-O-6</td>
<td>5</td>
<td>1.00</td>
<td>19</td>
<td>3.80</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>4</td>
<td>0.80</td>
<td>17</td>
<td>3.40</td>
</tr>
<tr>
<td>PF-O-8</td>
<td>9</td>
<td>1.80</td>
<td>14</td>
<td>2.80</td>
</tr>
<tr>
<td>PF-O-9</td>
<td>10</td>
<td>2.00</td>
<td>12</td>
<td>2.40</td>
</tr>
<tr>
<td>PF-O-10</td>
<td>9</td>
<td>1.80</td>
<td>15</td>
<td>3.00</td>
</tr>
</tbody>
</table>
Table 3-15. Reaction rates for Pos and Neg events.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>CAE Pos $(x10^3 \text{ mV s}^{-1})$</th>
<th>CAE Neg $(x10^3 \text{ mV s}^{-1})$</th>
<th>[iodine] Pos $(x10^2 \text{ M s}^{-1})$</th>
<th>[iodine] Neg $(x10^2 \text{ M s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-O-5</td>
<td>0.019 M</td>
<td>2.93±0.44</td>
<td>-2.58±0.34</td>
<td>25.6±1.4</td>
<td>-24.6±1.1</td>
</tr>
<tr>
<td>PF-O-6</td>
<td>0.023 M</td>
<td>3.29±0.39</td>
<td>-2.85±0.35</td>
<td>27.6±0.9</td>
<td>-33.2±1.3</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>0.026 M</td>
<td>4.13±0.37</td>
<td>-4.09±0.28</td>
<td>39.6±2.9</td>
<td>-35.9±2.7</td>
</tr>
<tr>
<td>PF-O-8</td>
<td>0.030 M</td>
<td>4.06±0.39</td>
<td>-3.95±0.35</td>
<td>51.4±3.6</td>
<td>-41.7±2.7</td>
</tr>
<tr>
<td>PF-O-9</td>
<td>0.034 M</td>
<td>12.3±0.9</td>
<td>-14.7±0.2</td>
<td>56.6±3.9</td>
<td>-42.4±2.0</td>
</tr>
<tr>
<td>PF-O-10</td>
<td>0.037 M</td>
<td>2.57±0.27</td>
<td>-2.67±0.24</td>
<td>102±4.7</td>
<td>-59.4±3.8</td>
</tr>
</tbody>
</table>

The average number of CAE d.c. peaks, 7±3, has actually decreased somewhat over the series PF-K (10±2), although the large error present in the first value makes conclusions difficult. The average number of peaks for the UV-Vis data, 15±2, remains the same as for the previous series (15±2), implying that the temperature increase has no effect on the number of peaks observed.

3.5.4.2 Peak Reaction Rates

The reaction rates for the pos and neg phases of the CAE d.c. and UV-Vis data are in Table 3-15. To assess the impact of the five degree increase in temperature, the rates in PF-K were compared to those presented here. The CAE d.c. rates increased as often as
they decreased. \textit{i.e.} an effect of temperature on rates was not observed. This suggests that under these conditions the rate at which dissolved oxygen is released from solution is already at its maximum.

Table 3-16. Iodine consumption/production ratios.

<table>
<thead>
<tr>
<th>Run</th>
<th>initial [iodate]</th>
<th>PF-K (consumption/production)</th>
<th>PF-O (consumption/production)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.019 M</td>
<td>0.808</td>
<td>1.20</td>
</tr>
<tr>
<td>6</td>
<td>0.023 M</td>
<td>0.940</td>
<td>0.907</td>
</tr>
<tr>
<td>7</td>
<td>0.026 M</td>
<td>0.992</td>
<td>0.811</td>
</tr>
<tr>
<td>8</td>
<td>0.030 M</td>
<td>0.754</td>
<td>0.749</td>
</tr>
<tr>
<td>9</td>
<td>0.034 M</td>
<td>0.647</td>
<td>0.582</td>
</tr>
<tr>
<td>10</td>
<td>0.037 M</td>
<td>1.04</td>
<td></td>
</tr>
</tbody>
</table>

For the UV-Vis data, the iodine production rates increased by an average of 2.9±0.5 times, while the consumption rates increased an average of 3.2±0.8 times. Between the series, however, the iodine production rate quickly outstrips the consumption rate. For example, in PF-O-9 (Table 3-16) the consumption rate has fallen to only one-half the production rate, suggesting that temperature increases favour iodine production over consumption.

The data clearly show that at the increased temperature, there is an initial emphasis on consumption of iodine in series PF-O. However, the production and
consumption rates come closest together at run 7 in PF-K (0.992) and run 6 in PF-O (0.907). After that point, the iodine production rate for the higher temperature series nearly doubles the consumption rate by the end of the experiment.

![Graph showing reaction rates for different initial iodate concentrations.](image)

**Figure 3-14. Reaction rates for different initial iodate concentrations.**

### 3.5.4.3 Extent of Reaction

The integrated CAE d.c. data are plotted separately for each run in Figure 3-15 (runs 1 to 6) and in Figure 3-16 (runs 7 to 10). The integrated CAE d.c. appears to be more sensitive to transitions in this series than to the previous series. In the first four runs where acoustic activity is due mostly to the catalytic decomposition of hydrogen
peroxide, the transitions appear to be random, with the exception of the transition at ca. 200 seconds. This suggests an acoustic event has occurred which is independent of the concentration of iodate. The differences in the slope of the line before and after the transition point further suggests that either another acoustically active process has begun, in addition to the previous process, or replacing the previous process. The former appears more likely. Chemically, the initial process is the catalytic decomposition of hydrogen peroxide. The second process is the termination of the free radical stage of iodine production.

Recall that iodine production in the BR oscillator is divided into stages: free radical production of HOIO and non-radical consumption of HOIO to ultimately form iodine. The first stage produces oxygen and only switches to the second stage when sufficient HOIO has been generated. This is the proposed sequence of events:

1. induction phase: iodate is consumed by reaction I3 to form intermediates HOIO and HOI. Oxygen evolution is primarily due to the catalytic decomposition of hydrogen peroxide.

2. iodine production (free radical): when sufficient HOIO has been produced, it is consumed by reaction I5 and a rapid chain reaction begins in the sequence I5, M1, M2, O2. The chain reaction continues for ca. 20 seconds before terminating. In that time, there is a large amount of oxygen evolved which appears on the integrated CAE d.c. trace as a sharp rise at ca. 200 seconds.

3. return to normal: step 2 was unable to produce sufficient HOIO to enable the switch to iodine production (reactions I2, D1 and I1). This is likely due to insufficient iodate.
Figure 3-15. Integrated CAE d.c. data for $t = 480$ seconds, runs 1 to 6.
The fifth run, PF-O-5, is itself a transition experiment. Semi-regular peaks are present in the raw CAE d.c. data suggesting the BR oscillator is active. Sharp transitions appear at ca. 400 seconds which the UV-Vis data indicates is the end of the oscillation period. The gas evolution at this time cannot be due to oscillations, but another process. Possibly the catalytic decomposition of hydrogen peroxide is again the main oxygen generator, this time unhindered by competing reactions. Assuming the limiting reagent is iodate, we again have the situation where there is insufficient iodate to produce HOIO and hence oscillations cease. However, there is still sufficient hydrogen peroxide and aqueous iodine to evolve oxygen.

Figure 3-16. Integrated CAE d.c. data for t = 480 seconds, runs 7 to 10.
The integrated CAE data for runs PF-O-6 through 10 generally all show a termination transition at ca. 400 seconds. Many of the remaining transitions can be attributed to features in the UV-Vis traces of the individual runs. The following table lists the transitions and interpretations for PF-O-6 through 8. Run PF-O-9 is more difficult to interpret as the integrated trace is an order of magnitude larger than previous runs. This has the effect of masking out the key transitions.

Table 3-17. Interpretation of transitions in integrated CAE d.c. data.

<table>
<thead>
<tr>
<th>Series</th>
<th>Transition Point (s)</th>
<th>Interpretation based on correlation with UV-Vis data.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-O-6</td>
<td>70-100</td>
<td>switch from induction phase to oscillations</td>
</tr>
<tr>
<td>PF-O-6</td>
<td>390-400</td>
<td>switch from oscillations to termination</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>60-80</td>
<td>switch from induction phase to oscillations</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>180-200</td>
<td>maximum amplitude oscillations</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>270-280</td>
<td>iodine production rate accelerates more quickly than consumption rate</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>380-400</td>
<td>switch from oscillations to termination</td>
</tr>
<tr>
<td>PF-O-7</td>
<td>460-480</td>
<td>not assigned</td>
</tr>
<tr>
<td>PF-O-8</td>
<td>40-50</td>
<td>switch from induction to irregular oscillations</td>
</tr>
<tr>
<td>PF-O-8</td>
<td>100-110</td>
<td>switch to regular oscillations</td>
</tr>
<tr>
<td>PF-O-8</td>
<td>180-200</td>
<td>maximum amplitude oscillations</td>
</tr>
<tr>
<td>PF-O-8</td>
<td>400-420</td>
<td>switch from oscillations to termination</td>
</tr>
</tbody>
</table>
Figure 3-17. Integrated CAE d.c. data at time = 480 s.

The above figure illustrates the integrated CAE d.c. data at time = 480 seconds. Similar to the previous series, there is a generally linear trend followed by a sharp increase. In this series the linear trend extends to 0.030 M iodate, whereas in the previous series, the linear trend extended to 0.0020 M iodate, the difference due to the five degree increase in temperature.
3.5.5 Series PF-O: Conclusions

There are significant temperature effects on all phases of the oscillator: peak amplitudes, pos and neg rates, as well as overall reaction rates.

The integrated CAE d.c. data demonstrated distinct transition events which were not initially seen in series PF-K. This may be due in part to both the increased temperature and a higher sampling frequency. In hindsight, some transitions can be seen in the previous series.

The transitions observed often heralded events present in the UV-Vis data, indicating that the CAE d.c. data is almost, but not quite, in phase with the UV-Vis data as we saw in the discussion of series PF-K. This has important consequences as we were unable to establish a phase relationship in this data series. Even a brief inspection of the data clearly suggests that no simple relationship is present. Yet this is a misleading conclusion, as increased gas evolution may be creating “macro” events (i.e. many bubbles bursting nearly simultaneously) which are displayed as one single broad peak. There may be no way of easily determining if several peaks are present where one is seen. One possibility is to increase the sampling rate, but the 200 ms time constant of the amplifier’s d.c. output limits our temporal resolution.
3.6 Series PF-T, iodate varied from 0.004 to 0.037 M, 35°C

This is the third and last of the iodate series. It uses the same basic experimental procedures as PF-O with two changes:

1. another five degree rise in temperature.
2. sampling period decreased from 3.0 seconds to 1.0 seconds

It was apparent from the previous series that the resolution of both the UV-Vis and CAE d.c. data needed improving. This would be even more true in an experiment with elevated temperatures as increased reaction rates would give rise to events which may be missed by existing sampling rates.

However, the control computers were already functioning near their limits and significant effort was required to re-write the control software to increase the system’s overall performance.

Table 3-18. Instrument parameters for series PF-T.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Sampling Period</th>
<th>Other settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAE d.c.</td>
<td>1.0 s</td>
<td>64 dB gain</td>
</tr>
<tr>
<td>scope</td>
<td>min. 1.5 s</td>
<td>1600 mV input range, 2.5 MHz digitization rate</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>1.0 s</td>
<td>300 to 600 nm; 2 nm resolution</td>
</tr>
</tbody>
</table>
3.6.1 Data Work-up

The raw data collected from the various instruments required some preprocessing before an analysis could be conducted. The work-up is identical to that described for the previous series.

3.6.2 PF-T-1 and 2

The data from PF-T-1 and 2 are presented in Figure C-20. PF-T-1 (initial [iodate] = 0.004 M) show no UV-Vis or acoustic activity.

PF-T-2 (initial [iodate] = 0.008 M), clearly shows the noise due to bubbles in the light path. The CAE trace shows a little more activity than for PF-T-1.

3.6.3 PF-T-3 and 4

In PF-T-3 (initial [iodate] = 0.011 M) and PF-T-4 (initial [iodate] = 0.015 M), show peaks of an irregular shape and distribution indicating extensive bubble evolution, rather than iodine absorption.
3.6.3.1 Autocorrelation

The autocorrelograms of series PF-T-1 through 4 (Figure 3-18) present no surprises. The time constants of the periodicities generally increase as iodate concentration increases. The periodicity of PF-T-1 is unclear. PF-T-2 shows strong periodicity with a time constant of ca. 16 seconds. PF-T-3 exhibits less forceful periodicity of ca. 18 seconds while PF-T-4 presents a tenuous periodicity of ca. 27 seconds. Series PF-T-5 through 10 show no significant periodicity and so are not illustrated.

3.6.4 PF-T-5 through 10

The initial iodate concentrations studied are T-5 (0.019 M), T-6 (0.023 M), T-7 (0.026 M), T-8 (0.030 M), T-9 (0.034 M), and T-10 (0.037 M).
Figure 3-18. Autocorrelograms of CAE d.c. data for series PF-T-1 through 4. The time constant (τ) is one second.
3.6.4.1 Peak Count and Frequency

The data from runs 5 through 10 are shown in the following figures. The UV-Vis trace for PF-T-5 confirms our earlier suspicions that run 5 is a transition run - a border between non-osc. and osc. conditions - showing some signs of oscillations, but not forming the sawtooth peaks associated with regular oscillations. The remaining UV-Vis traces take on a skewed sawtooth appearance implying that the iodine production rates are faster than the iodine consumption rates. Several trends are more easily seen in Table 3-19. The average number of CAE d.c. peaks, 11±1, is representative of the previous series (10±2 and 7±3). The average number of UV-Vis peaks, 15±2, is also similar to the previous series (15±2 and 15±2). These results provide strong evidence that the number of peaks observed in the time period from 100 to 400 seconds is independent of temperature, implying that the mechanistic steps responsible for switching the oscillator between its two steady states are also independent of temperature under these conditions. These steps are discussed further in Chapter Five.
Table 3-19. Peak parameters for Series PF-T.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>CAE d.c. Number of peaks</th>
<th>CAE d.c. Number of peaks/min.</th>
<th>UV-Vis Number of peaks</th>
<th>UV-Vis Number of peaks/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-T-5</td>
<td>0.019 M</td>
<td>10</td>
<td>2.00</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PF-T-6</td>
<td>0.023 M</td>
<td>12</td>
<td>3.20</td>
<td>16</td>
<td>3.20</td>
</tr>
<tr>
<td>PF-T-7</td>
<td>0.026 M</td>
<td>11</td>
<td>2.20</td>
<td>15</td>
<td>3.00</td>
</tr>
<tr>
<td>PF-T-8</td>
<td>0.030 M</td>
<td>11</td>
<td>2.20</td>
<td>15</td>
<td>3.00</td>
</tr>
<tr>
<td>PF-T-9</td>
<td>0.034 M</td>
<td>12</td>
<td>2.40</td>
<td>12</td>
<td>2.40</td>
</tr>
<tr>
<td>PF-T-10</td>
<td>0.037 M</td>
<td>7</td>
<td>1.40</td>
<td>11</td>
<td>2.20</td>
</tr>
</tbody>
</table>

Table 3-20. Reaction rates for Pos and Neg events.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [iodate]</th>
<th>CAE d.c. Pos (x10³ mV·s⁻¹)</th>
<th>CAE d.c. Neg (x10³ mV·s⁻¹)</th>
<th>[iodine] Pos (x10² M·s⁻¹)</th>
<th>[iodine] Neg (x10² M·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-T-6</td>
<td>0.023 M</td>
<td>3.31±0.19</td>
<td>-3.15±0.20</td>
<td>86.4±6.5</td>
<td>-67.1±2.0</td>
</tr>
<tr>
<td>PF-T-7</td>
<td>0.026 M</td>
<td>4.48±0.46</td>
<td>-4.60±0.38</td>
<td>114±5</td>
<td>-78.5±3.4</td>
</tr>
<tr>
<td>PF-T-8</td>
<td>0.030 M</td>
<td>3.98±0.29</td>
<td>-4.37±0.22</td>
<td>154±2</td>
<td>-93.4±5.8</td>
</tr>
<tr>
<td>PF-T-9</td>
<td>0.034 M</td>
<td>6.18±0.38</td>
<td>-5.60±0.36</td>
<td>194±8</td>
<td>-103±7</td>
</tr>
<tr>
<td>PF-T-10</td>
<td>0.037 M</td>
<td>4.57±0.36</td>
<td>-4.36±0.41</td>
<td>296±16</td>
<td>-181±9</td>
</tr>
</tbody>
</table>
The trends observed in the above table’s data generally reflect the trends observed in the previous two series:

1. **CAE d.c. maximum number of peaks**: the previous two series (PF-K and -O) show the maximum number to be at $[\text{iodate}] = 0.034 \text{ M}$. In this series, the maximum occurs at both $[\text{iodate}] = 0.023 \text{ M}$ and $0.034 \text{ M}$. This was the expected result, as increasing the iodate concentration should increase the number of observed peaks. Except for this one result, however, inspection of the data in the table shows an almost random number of peaks occurring at any particular concentration. We attribute these “random” numbers to the presence of “macro” events which were discussed above. To briefly recap, macro events occur when a large number of gas bubbles burst within the sampling period. This results in a single broad peak instead of several distinct peaks. Thus in any particular experimental run, it is difficult to estimate the true number of peaks.

2. **UV-Vis maximum number of peaks**: the first series (PF-K) shows the maximum number to be at $[\text{iodate}] = 0.037 \text{ M}$. The next two series place the maximum at $[\text{iodate}] = 0.023 \text{ M}$. This trend is misleading as we are only counting the number of peaks which occur between 100 and 400 seconds. Closer inspection of the raw data reveals the fact that the induction period *decreases* as iodate concentration increases. This observation has been made earlier in this work, but the data resolution had been insufficient to accurately determine when oscillations began. Taking into account all the observed oscillations, the maximum number could be placed at $[\text{iodate}] = 0.037 \text{ M}$.

In the next table, we examine the reaction rates of the *pos* and *neg* events in the CAE d.c. and UV-Vis data.
3.6.4.2 Peak Reaction Rates

The reaction rates for the pos and neg phases of the CAE d.c. and UV-Vis data are in Table 3-20. There is a large temperature effect which will be discussed in later sections. We note here only the common trends between the three experimental series:

1. Close correlation between pos and neg rates for CAE d.c. data in this series. Unlike the iodine data, the CAE d.c. data have a high degree of correlation between the two event rates at all the concentrations studied. This observation implies that the pos event corresponds to the production of a species while the neg event corresponds to the non-production of a species (i.e. O₂), rather than consumption. Hence, a CAE d.c. peak should have the same general shape regardless of the exact reaction rates. For the UV-Vis, the peak shapes will vary as the neg event in this case corresponds to iodine consumption, and the rate of iodine consumption varies with iodate concentration.

2. CAE d.c. maximum rates occur at [iodate] = 0.034 M, regardless of temperature. This is the expected trend that rates should increase as concentration increases. This observation further indicates that the “macro” events discussed above produce peaks with slopes which are still representative of the acoustic processes. As an aside, it should be noted that a “local maxima” of reaction rates occurs at [iodate] = 0.026 M in each series at this temperature.

3. The iodine consumption/production ratios generally decrease as iodate concentration increases (Table 3-21) and as temperature increases. Under maximum conditions (initial [iodate] = 0.037 M, temperature = 35°C) the consumption rate shrank to ca. one-half the production rate.
Table 3-21. Iodine consumption/production ratios.

<table>
<thead>
<tr>
<th>Run</th>
<th>initial [iodate] (M)</th>
<th>PF-K (consumption/production)</th>
<th>PF-O (consumption/production)</th>
<th>PF-T (consumption/production)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.023 M</td>
<td>0.940</td>
<td>1.20</td>
<td>0.777</td>
</tr>
<tr>
<td>7</td>
<td>0.026 M</td>
<td>0.992</td>
<td>0.907</td>
<td>0.689</td>
</tr>
<tr>
<td>8</td>
<td>0.030 M</td>
<td>0.754</td>
<td>0.811</td>
<td>0.606</td>
</tr>
<tr>
<td>9</td>
<td>0.034 M</td>
<td>0.647</td>
<td>0.749</td>
<td>0.531</td>
</tr>
<tr>
<td>10</td>
<td>0.037 M</td>
<td>1.04</td>
<td>0.582</td>
<td>0.611</td>
</tr>
</tbody>
</table>

Figure 3-19. Reaction rates for different initial iodate concentrations.
3.6.4.3 Extent of Reaction

The integrated CAE d.c. data are plotted separately for the strongly oscillating runs (6 through 9) in Figure 3-20. The integrated CAE d.c. data generally show a
Table 3-22. Interpretation of transitions in integrated CAE d.c. data.

<table>
<thead>
<tr>
<th>Series</th>
<th>Transition Point (s)</th>
<th>Interpretation based on correlation with UV-Vis data.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-T-6</td>
<td>140-150</td>
<td>switch from induction phase to oscillations</td>
</tr>
<tr>
<td>PF-T-6</td>
<td>350-360</td>
<td>switch from oscillations to termination</td>
</tr>
<tr>
<td>PF-T-7</td>
<td>140-150</td>
<td>switch from induction phase to oscillations</td>
</tr>
<tr>
<td></td>
<td>190-200</td>
<td>maximum amplitude oscillations</td>
</tr>
<tr>
<td>PF-T-7</td>
<td>280-290</td>
<td>iodine production rate accelerates more quickly than</td>
</tr>
<tr>
<td></td>
<td>370-380</td>
<td>consumption rate</td>
</tr>
<tr>
<td>PF-T-8</td>
<td>80-90</td>
<td>switch from induction phase to oscillations</td>
</tr>
<tr>
<td>PF-T-8</td>
<td>280-290</td>
<td>iodine production rate accelerates more quickly than</td>
</tr>
<tr>
<td></td>
<td>320-330</td>
<td>consumption rate</td>
</tr>
<tr>
<td>PF-T-9</td>
<td>80-170</td>
<td>see discussion</td>
</tr>
<tr>
<td>PF-T-9</td>
<td>320-330</td>
<td>switch from oscillations to termination</td>
</tr>
</tbody>
</table>

termination transition at ca. 400 seconds. Many of the remaining transitions can be attributed to features in the UV-Vis traces of the individual runs. Table 3-22 lists the transitions and interpretations for PF-T-6 through 9.

The transition times given in the table generally precede the observed event by ca. 20 seconds, which is the time constant seen in the autocorrelogram results. The PF-T-9 transition at time = 80 seconds is difficult to interpret. Rather than a sharp transition
point, a long, slight rise is observed which lasts ca. 90 seconds. One explanation may be that the oxygen bubbles are bursting at their maximum rate during this time period. This may be a limit of the experimental system (i.e. cell geometry) rather than a chemical effect.

Figure 3-21. Integrated CAE d.c. data at time = 480 s.

The above figure illustrates the integrated CAE d.c. data at time = 480 seconds. The data presented is the culmination of a trend observed in previous series where the linear portion of the curve was increasing at the expense of the non-linear portion. In this series, the linear portion (slope = 433 mV·s⁻¹, \( r^2 = 0.974 \)) dominates to the exclusion of the non-linear portion. That is, temperature is speeding up the overall oxygen evolution of the system to the extent that oxygen is forming bubbles at its maximum rate at the highest
temperature, 35°C. Note that this trend has also been observed for the rates of the pos and neg events.
3.6.5 Series PF-T: Conclusions

The increased sampling rate provided better resolution of the UV-Vis data, which substantially aided the data analysis and interpretation. The single most important discovery was that an initial \([\text{iodate}] = 0.019 \text{ M}\) was not sufficient to produce iodine oscillations in some cases. We conclude that this is a borderline concentration and any data collected may reveal oscillatory information as often as not.

Autocorrelograms of non-oscillatory data revealed a periodicity which increased as iodate concentration increased. The source of oscillations is believed to be from the build-up and release of dissolved oxygen as discussed for the previous series. The time constant at \([\text{iodate}] = 0.008 \text{ M}\) was ca. 16 seconds, at 0.011 M was ca. 18 seconds and at 0.015 M was ca. 27 seconds. Autocorrelograms of oscillatory data showed no detectable periodicity.

The maximum number of CAE d.c. peaks observed occurred at \([\text{iodate}] = 0.034 \text{ M}\), again reflecting the difficulty of obtaining reliable data for \([\text{iodate}] = 0.037 \text{ M}\). This appears to be a valid observation as all three experimental series corroborate this observation.

The CAE d.c. data showed close correlation of the absolute values of the \(\text{pos}\) and \(\text{neg}\) rates regardless of \([\text{iodate}]\). This is unique from the UV-Vis data which shows the \(\text{pos}\) (iodine production) rate increases while the \(\text{neg}\) (iodine consumption) rate decreases as \([\text{iodate}]\) increases. The conclusion is that the CAE d.c. \(\text{pos}\) rate is related to production of a species while the \(\text{neg}\) rate is related to \textit{non}-production, not consumption of a species. This is further evidence that gas evolution is the dominant process responsible for CAE in the BR oscillator.
The integrated CAE d.c. data showed similar transitions as the previous series (PF-O). The integrated CAE d.c. at the end of the experiments (time = 480 s.) exhibited a strictly linear trend, unlike the previous series which demonstrated a linear trend followed by a sharp second order rise.

Again, the quality of these integrated CAE d.c. measurements suggest analytical potential.
Chapter Four - Hydrogen Peroxide Study

“How come I get all the hard questions?”

- O. North

4.1 Introduction

One of the conclusions from the series in the previous chapter is that hydrogen peroxide plays an important role in the production of oxygen in the Briggs-Rauscher oscillator. The aim of this experimental series is to use the “high resolution” system presented in the last chapter to monitor the effect of varying the concentration of H$_2$O$_2$.

The experimental conditions are the same as detailed in the previous series with the exception that H$_2$O$_2$ is varied instead of iodate.
4.2 Series PF-S, Hydrogen Peroxide varied from 0.078 to 0.78 M, 35°C

4.2.1 Data Work-up

The raw data collected from the various instruments required some preprocessing before an analysis could be conducted. The work-up is identical to that described for the previous series.

4.2.2 PF-S-1 and 2

PF-S-1, initial \([\text{H}_2\text{O}_2] = 0.078\) M, exhibits a data trace (Figure C-24) similar to PF-T-5 of the previous series. The most noticeable difference is that both the UV-Vis and the CAE peaks begin the experiment with relatively large amplitudes and finish the experiment with relatively small amplitudes. The data suggests that rapid catalytic decomposition of \(\text{H}_2\text{O}_2\) is occurring, consuming the \(\text{H}_2\text{O}_2\) until it is depleted.

The UV-Vis trace in PF-S-2 (initial \([\text{H}_2\text{O}_2] = 0.16\) M) shows large, broadly skewed peaks, indicating high iodine production rates and low iodine consumption rates. Interestingly, the CAE peaks have all but disappeared, leading to the conclusion that the

| Table 4-1. Instrument parameters for series PF-S. |
|----------------|----------------|
| Instrument     | Samp. Period  | Other settings                        |
| CAE d.c.       | 1.0 s         | 64 dB gain                             |
| scope          | min. 1.5 s    | 1600 mV input range, 2.5 MHz digitization rate |
| UV-Vis         | 1.0 s         | 300 to 600 nm; 2 nm resolution         |
non-oscillatory process responsible for CAE in PF-S-1 has been replaced. This new process, part of the oscillator, favours iodine production over iodine consumption and also over oxygen production.

4.2.3 PF-S-3 and 4

The UV-Vis data of PF-S-3 (initial [H₂O₂] = 0.24 M) and PF-T-4 (initial [H₂O₂] = 0.31 M), show the beginnings of a trend. As initial [H₂O₂] increases, the broadly skewed peaks are being replaced by the needle-shaped peaks seen in previous series. More importantly, the needle-shaped peaks occur at the beginning of the experiment, when [H₂O₂] is greatest. The broadly skewed peaks occur towards the end of the experiment when [H₂O₂] is lowest. By analogy, we can conclude that the broad peaks observed at the end of the experiments in the previous series are the result of low [H₂O₂] rather than low [iodate].

4.2.3.1 Autocorrelation

The autocorrelograms for series PF-S-1 through 4 are in Figure 4-1. PF-S-1 shows the beginnings of periodicity, indicating this is a “transition” series similar to the PF-x-5 series seen earlier. PF-S-2 has distinct periodicity with a time constant equal to 16τ, or 32 seconds. PF-S-3 also exhibits periodicity with a time constant of 40 seconds. PF-S-4 and the following series, in which the broadly skewed peaks are replaced by needle-shaped peaks, show no distinct periodicity. This suggests that the periodicity is tied to the non-
oscillatory processes which generate CAE at low $[\text{H}_2\text{O}_2]$, and these processes are not favoured as $[\text{H}_2\text{O}_2]$ increases.
Figure 4-1. Autocorrelograms of CAE d.c. data for series PF-S-1 through 4. The time constant (τ) is two seconds.
4.2.4 PF-S-5 through 10

The initial $[\text{H}_2\text{O}_2]$ studied is S-5 (0.39 M), S-6 (0.47 M), S-7 (0.55 M), S-8 (0.63 M), S-9 (0.71 M), and S-10 (0.78 M).

4.2.4.1 Peak Count and Frequency

The data from runs 5 through 10 are shown in the Figures C-26 through C-28. The UV-Vis traces clearly indicate that as initial $[\text{H}_2\text{O}_2]$ increases, the iodine production and consumption rates increase producing the familiar “needle-shaped” peaks.

Table 4-2. Peak parameters for Series PF-S.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial $[\text{H}_2\text{O}_2]$</th>
<th>CAE d.c. Number of peaks</th>
<th>UV-Vis Number of peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-S-2</td>
<td>0.16 M</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>PF-S-3</td>
<td>0.24 M</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>PF-S-4</td>
<td>0.31 M</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>PF-S-5</td>
<td>0.39 M</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>PF-S-6</td>
<td>0.47 M</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>PF-S-7</td>
<td>0.55 M</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>PF-S-8</td>
<td>0.63 M</td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>PF-S-9</td>
<td>0.71 M</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>PF-S-10</td>
<td>0.78 M</td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>
The CAE d.c. peak data shows no correlation between the number of peaks observed and initial \([\text{H}_2\text{O}_2]\), with the average number of peaks between 100 and 400 seconds to be 10±1. In contrast, the UV-Vis data shows the number of peaks increasing as initial \([\text{H}_2\text{O}_2]\) increases. The average number of peaks is 11±2. Therefore, the UV-Vis is not detecting just bubbles. The acoustically active process must be independent of \([\text{H}_2\text{O}_2]\).

Table 4-3. Reaction rates for \(\text{Pos}\) and \(\text{Neg}\) events.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial [(\text{H}_2\text{O}_2)]</th>
<th>CAE d.c. (\text{Pos}) (\times10^3\text{mV} \cdot \text{s}^{-1})</th>
<th>CAE d.c. (\text{Neg}) (\times10^3\text{mV} \cdot \text{s}^{-1})</th>
<th>[iodine] (\text{Pos}) (\times10^2\text{M} \cdot \text{s}^{-1})</th>
<th>[iodine] (\text{Neg}) (\times10^2\text{M} \cdot \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-S-2</td>
<td>0.16 M</td>
<td>0.93±0.04</td>
<td>-0.89±0.06</td>
<td>239±8</td>
<td>-52.1±6.2</td>
</tr>
<tr>
<td>PF-S-3</td>
<td>0.24 M</td>
<td>3.30±0.21</td>
<td>-3.29±0.23</td>
<td>422±16</td>
<td>-52.3±2.5</td>
</tr>
<tr>
<td>PF-S-4</td>
<td>0.31 M</td>
<td>6.12±0.78</td>
<td>-5.88±0.76</td>
<td>330±10</td>
<td>-38.2±1.8</td>
</tr>
<tr>
<td>PF-S-5</td>
<td>0.39 M</td>
<td>3.66±0.30</td>
<td>-3.28±0.32</td>
<td>295±15</td>
<td>-55.3±2.1</td>
</tr>
<tr>
<td>PF-S-6</td>
<td>0.47 M</td>
<td>3.16±0.21</td>
<td>-3.26±0.26</td>
<td>244±5</td>
<td>-83.4±5.1</td>
</tr>
<tr>
<td>PF-S-7</td>
<td>0.55 M</td>
<td>2.69±0.12</td>
<td>-2.60±0.16</td>
<td>413±9</td>
<td>-82.2±2.4</td>
</tr>
<tr>
<td>PF-S-8</td>
<td>0.63 M</td>
<td>2.37±0.13</td>
<td>-2.28±0.12</td>
<td>303±15</td>
<td>-96.1±2.0</td>
</tr>
<tr>
<td>PF-S-9</td>
<td>0.71 M</td>
<td>3.13±0.24</td>
<td>-3.19±0.22</td>
<td>286±14</td>
<td>-87.0±3.5</td>
</tr>
<tr>
<td>PF-S-10</td>
<td>0.78 M</td>
<td>3.27±0.19</td>
<td>-3.30±0.18</td>
<td>308±10</td>
<td>-60.1±1.7</td>
</tr>
</tbody>
</table>
4.2.4.2 Peak Reaction Rates

The reaction rates for the pos and neg phases of the CAE d.c. and UV-Vis data are in Table 4-3 and depicted graphically in Figure 4-2. The CAE d.c. data presents no surprises as it shows an initial period of instability before settling down to a near linear trend for both the pos and neg rates. As mentioned in previous discussions, there is a close correlation between the pos and neg rates - the average neg/pos ratio is 0.978±0.041.

The UV-Vis data exhibits interesting behaviour. The iodine production rates appear to oscillate with increasing H₂O₂. This trend is also seen in Cooke’s data³⁰, but to a lesser extent. The iodine consumption rates are nearly linear, again in agreement with Cooke. Unlike the previous iodate series, the consumption / production ratios are much lower - the average is 0.271±0.070.
Figure 4-2. Reaction rates for different initial \( \text{H}_2\text{O}_2 \) concentrations.

### 4.2.4.3 Extent of Reaction

The integrated CAE d.c. data for series PF-S-1 through 6 are plotted in Figure 4-3 and for series PF-S-7 through 10 in Figure 4-4. Numerical analysis of the data curves revealed the following facts:

PF-S-1. This pre-oscillation series fit best to a first order function with \( k = 3.88 \times 10^3 \text{ s}^{-1} \), \( r^2 = 0.997 \) and \( see = 0.185 \), suggesting that catalytic decomposition of \( \text{H}_2\text{O}_2 \) is the primary CAE process.
PF-S-2. The data from this series provided a linear fit with slope = 0.01, \( r^2 = 0.998 \) and 
\( see = 0.072 \). We suggest that at this \([\text{H}_2\text{O}_2]\) (the minimum necessary for oscillations),
there is competition for the \( \text{H}_2\text{O}_2 \) between the oscillatory and non-oscillatory processes
resulting in a pseudo-stationary state where the rate of oxygen evolution appears constant.

PF-S-3 shows the beginnings of a second order function of the form discussed earlier. The fit resulted in \( k = 4.91 \times 10^{-4} \text{ mV}^{-1} \text{s}^{-1} \), \( r^2 = 0.998 \) and \( see = 0.136 \).

PF-S-4 also fits well to the same second order function with \( k = 3.97 \times 10^{-3} \text{ mV}^{-1} \text{s}^{-1} \),
\( r^2 = 0.988 \) and \( see = 0.237 \).

PF-S-5 is the first of the series with multiple distinct transition events. It is extremely
difficult to curve fit data of this nature. We experienced similar difficulties with PF-S-6.

PF-S-7 through PF-S-10 all fit best to the second order function described above. The
parameters are in Table 4-4.
Beginning with PF-S-5, transition events can be seen which correspond to events observed in the UV-Vis data. Unlike previous series, the acoustic events are in phase with the iodine events - there is no time shift. For example, in PF-S-5 we observe transition
events at 240 seconds (max. peak amplitude), 330 seconds (last regular oscillation) and 400 seconds (termination of oscillations).

We conclude that if $[\text{H}_2\text{O}_2]$ is low (but high enough to provide regular oscillations), the oscillatory mechanism competes for $\text{H}_2\text{O}_2$ more efficiently than the non-oscillatory mechanism. This results in a smooth, second order rise of integrated CAE d.c. data. Since in the oscillatory mechanism oxygen is evolved only during the iodine production stage, the CAE events will be in phase with the iodine events.

Table 4-4. Second order curve fit results for integrated CAE d.c. data.

<table>
<thead>
<tr>
<th>Series</th>
<th>initial $[\text{H}_2\text{O}_2]$</th>
<th>$k$ (mV$^{-1}$s$^{-1}$)</th>
<th>$r^2$</th>
<th>see</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF-S-7</td>
<td>0.55 M</td>
<td>$3.15 \times 10^{-4}$</td>
<td>0.997</td>
<td>0.133</td>
</tr>
<tr>
<td>PF-S-8</td>
<td>0.63 M</td>
<td>$2.90 \times 10^{-4}$</td>
<td>0.998</td>
<td>0.104</td>
</tr>
<tr>
<td>PF-S-9</td>
<td>0.71 M</td>
<td>$9.25 \times 10^{-5}$</td>
<td>0.998</td>
<td>0.098</td>
</tr>
<tr>
<td>PF-S-10</td>
<td>0.78 M</td>
<td>$2.40 \times 10^{-4}$</td>
<td>0.996</td>
<td>0.157</td>
</tr>
</tbody>
</table>

If $[\text{H}_2\text{O}_2]$ is high, both mechanisms receive sufficient $\text{H}_2\text{O}_2$ to generate oxygen gas. The steady oxygen evolved by the non-oscillatory mechanism inhibits the switching ability of the oscillatory mechanism resulting in a delay between moving from iodine consumption to production. The switch cannot occur until sufficient dissolved oxygen is removed from the reaction mixture.
Figure 4-4. Integrated CAE d.c. data for PF-S-7 through 10.
4.2.5 Series PF-S: Conclusions

The data from PF-S-1 and 2 illustrate the different processes responsible for CAE. In PF-S-1, the non-oscillatory catalytic decomposition of hydrogen peroxide is the main process generating the bubbles whose bursting is detected by CAE. In PF-S-2, the iodine production stage of the oscillator is the primary bubble nucleation process.

The UV-Vis peaks (where oscillations are observed) begin the reaction as sharp, needle shaped peaks and end the reaction as broadly skewed peaks implying that low \([H_2O_2]\) favours iodine production over consumption.

Autocorrelation analysis of the CAE d.c. data uncovered periodicity in those series where the system was oscillating weakly, or not at all. This is consistent with the observations made in the iodate series. The time constant of the periodicity varied from 32 to 40 seconds. In contrast, the iodate series (with \([H_2O_2]\) fixed at ca. 0.78M) posted time constants in the range 16 to 27 seconds. This suggests that periodicity is inversely proportional to the \([H_2O_2]\), which supports Wentzell's dissolved oxygen model. That is, assuming that the rate of oxygen evolution is proportional to \([H_2O_2]\), at low concentrations it would take a longer period of time for the dissolved oxygen to reach its solubility limit and commence bubble formation.

The number of CAE d.c. peaks observed (10±1) was mostly independent of initial \([H_2O_2]\). The number of UV-Vis peaks (11±2) was directly proportional to initial \([H_2O_2]\).

The CAE d.c. data showed close correlation of the absolute values of the pos and neg rates independent of initial \([H_2O_2]\). This is unique from the UV-Vis data which shows the pos (iodine production) rate oscillates while the neg (iodine consumption) rates show little variation.
The integrated CAE d.c. data showed similar transitions as the previous iodate series (PF-O and PF-T). In contrast, these transitions occurred mostly in phase with the iodine events rather than out of phase as observed for the iodate series. We conclude that the oscillatory mechanism competes for $\text{H}_2\text{O}_2$ more effectively than the non-oscillatory mechanism.
Chapter Five- Conclusions

“Life is full of little surprises.”
- Pandora

5.1 Proposed Skeleton Mechanism of the BR Oscillator

Both the CAE and the UV-Vis data show that the BR oscillator moves between two steady states: iodine production and iodine consumption.

5.1.1 Iodine Production

Step I5 initiates the radical processes which then produces HOIO autocatalytically. The experimental rate constants are not available for I5 or M1 although they have been estimated at $1.5 \times 10^4 \, \text{M}^{-2}\text{s}^{-1}$ and $1.0 \times 10^4 \, \text{M}^{-1}\text{s}^{-1}$ by Furrow and Noyes$^{32}$. Step M2’s rate$^{65}$ is on the order of $10^4$ at 25°C and that for step O2 is $7.5 \times 10^5 \, \text{M}^{-1}\text{s}^{-1}$ at 25°C$^{66}$. This suggests that I5 will be the rate limiting step, and the oxygen evolved in step O2 will be representative of the consumption of iodate to form HOIO.

The autocatalytic production of HOIO described above would carry on indefinitely if not for the presence of step I2 which becomes energetically favoured when HOIO and I$^\text{-}$ are at acceptably high levels. Both this step and step I1 are expected to be rapid in comparison to D1. Since step D1 evolves oxygen, the CAE produced should be in phase with the production of iodine. However, the phase relationships observed in
series PF-G-3 in Chapter Three indicate that the CAE is slightly out of phase with iodine production. We postulate that the slight delay is due to Wentzell's diffused oxygen model, discussed earlier.

5.1.2 Iodine Consumption

The oscillator switches from iodine production to consumption when iodide ion is low enough to make step C4 more favourable than step I1. During consumption, no oxygen is evolved, and so the rate of decrease of CAE will parallel the decrease of \( I_2 \).

The nine elementary steps proposed for this mechanism were first introduced by Furrow and Noyes\(^{32}\) in 1982, who initially proposed a total of 30 steps. Numerical modelling selected 10 steps as a necessary and sufficient set to account for the oscillatory dynamics. The other 19 steps may of course occur. The step we did not include in our mechanism is

\[ I_4. \quad 2\text{HOIO} \rightarrow \text{IO}^- + \text{HIO} + \text{H}^+ \]

This step is a two-equivalent reduction of iodine, implying that it should lie with the other two-equivalent processes in the non-radical iodine production stage. However, steps I2, D1 and I1 adequately explain the experimental observations without invoking another step, and so I4 is discarded. This assertion will need to be tested via numerical modelling to see if the model can be made to oscillate without I4.

In 1992, Turyani\(^{67}\) applied principal components analysis to the rate sensitivity matrix of the BR oscillator. A particular species was considered redundant if the omission of all of its consuming reactions had no significant effect on the calculated concentrations of important species. Using this system, Turyani reduced the number of mechanistic steps
to 8. This is close to our proposed mechanism with the exception that step O2 has been omitted.

5.1.3 Reaction Scheme

**FREE RADICAL PRODUCTION OF HOIO:**

D3. \( H^+ + IO^- + H_2O_2 \rightarrow HOIO + H_2O + O_2 \)

I5. \( H^+ + IO^- + HOIO \rightarrow 2IO^* + H_2O \)

M1. \( IO^* + H_2O + Mn^{2+} \leftrightarrow HOIO + Mn(OH)^{2+} \)

M2. \( Mn(OH)^{2+} + H_2O_2 \rightarrow H_2O + Mn^{2+} + HOO^* \)

O2. \( 2HOO^* \rightarrow H_2O_2 + O_2 \)

**CONSUMPTION OF HOIO TO FORM I2:**

I2. \( HOIO + I^- + H^+ \rightarrow 2HOI \)

D1. \( HOI + H_2O_2 \rightarrow I^- + O_2 + H^+ + H_2O \)

I1. \( HOI + I^- + H^+ \leftrightarrow I_2 + H_2O \)

**CONSUMPTION OF I2:**

C4. \( enol + I_2 \rightarrow RI + I^- + H^+ \)

I3. \( I^- + IO^- + 2H^+ \rightarrow HOIO + HOI \)
5.2 The Rate Limiting Step

There has been some question in the literature as to which step in the BR oscillator is rate limiting. Reaction C4, the iodide abstraction by the organic substrate, has a rate constant estimated at 40 M\(^{-1}\)s\(^{-1}\) based on work with the methylmalonic acid variation of the BR oscillator\(^{68}\). The currently accepted rate constant for reaction D1, the reduction of HOI to I\(_2\), is 37 M\(^{-1}\)s\(^{-1}\), determined by Liebhafsky\(^{62}\). More recently, Furrow studied reaction D1 under low-light conditions\(^{69}\) with periodic sampling by UV-Vis spectroscopy and published a rate constant of 3 ± 2 M\(^{-1}\)s\(^{-1}\).

Reaction D1 is the main oxygen evolving step of the BR oscillator and hence seemed a good candidate to study with CAE. In Chapter Two of this work, reaction D1 was studied under pseudo first order conditions and a rate constant of 1 ± 5 s\(^{-1}\) obtained.

Direct comparison of rate constants is difficult when they are of different reaction orders. Estimations could be made based on time to half-peak-height, for example, but researchers generally do not publish the raw data necessary to make those calculations. Another alternative would be to numerically integrate the proposed models, an option we briefly discuss in Chapter Six - Further Work.

Despite the shortcomings mentioned above, we believe that it is safe to conclude that reaction D1 is the rate limiting step in the BR oscillator.
5.3 CAE as an Analytical Tool to Study Oscillating Reactions

From the outset of this work, one of the goals was to develop an experimental system utilizing CAE which could deliver useful chemical information.

CAE has general attributes which make it useful for studying chemical systems which result in phase changes, gas evolution, crystal fracture, etc.. From an experimental standpoint CAE offers these benefits:

*non-invasive*: the BR oscillator is extremely sensitive not only to other halides, but also to physical conditions such as light and stirring. The non-invasive nature of CAE made it ideal to study this reaction.

*simple calibration*: CAE transducers are calibrated without removing them from the reaction vessel by attaching a second transducer to the reaction vessel and delivering a continuous signal from a signal generator.

In this work, CAE helped our understanding of the BR oscillator. Some of the conclusions we were able to draw are detailed in the following paragraphs.

In Chapter Two, the preliminary studies revealed that two processes were taking place in the induction. The *neg* phases were found to be independent of reagent concentration which suggested that a *neg* phase was in fact *non*-production of oxygen and that the oxygen was leaving the system through physical processes rather than being consumed in other reactions. The *pos* phase exhibited second order function behaviour; a foreshadowing of the second order behaviour which will be uncovered in the detailed studies and which confirmed step D1 as second order.

An attempt was made to isolate the CAE processes involved through the application of multivariate statistics on the a.c. signal data. The computed averaged
power spectra uncovered some structure in the frequency domain which led to the division of the spectra into two distinct regions: reaction activity and transducer signature.

Descriptor analysis of the a.c. signal data correctly predicted which signals belonged to a valid experimental run, and which belonged to a noise run. Principal components analysis failed to uncover any underlying structure of the data. Non-heirarchical clustering also failed to uncover further structure.

In Chapter Three, the detailed studies provided supporting evidence for the conclusions drawn in Chapter Two. The studies also uncovered the influence of temperature on oxygen evolution, correlated transition events in the integrated CAE data to events in the UV-Vis data, and discovered the presence of periodicity which has been unreported in the literature.

Despite the natural variability of CAE processes, several examples of useful quantitative relationships between integrated CAE and chemical concentrations were obtained. This bodes well for future analytical use of the technology. However, with all the advantages of CAE, there have also been some difficulties. Within-run reproducibility is poor, and significant errors accompany most calculations. The a.c. signals require considerable resources to acquire and store. Multivariate analysis produced few tangible results because of the single CAE production mechanism (gas evolution) studied.

Despite the shortcomings of this new technology, we believe that the utility of CAE as a tool for quantitative chemical analysis has been amply demonstrated in this exploratory work.
Chapter Six - Further Work

"The best laid plans often go fowl."

- W.E. Coyote

The difficulty with a first thesis in an area of experimental chemical exploration is that it often raises more questions than it can answer. The work presented here is no different. More experimenting at different temperatures and varying the other reagents in the system would provide excellent groundwork for answering the following questions.

What is a "shoulder event"?

We came across shoulder events in Chapter Two. They were observed many times in these experiments and appeared to be a phenomenon whereby the oscillator switched from state A to state B, only to switch back to A again after a few seconds. Since this event is unreported in the literature, it can only be answered by further CAE experimenting in conjunction with other in situ spectroscopic techniques.

Luminescence

Since the BR oscillator gives rise to high-frequency acoustic waves detectable by CAE, there is the possibility that these waves are also producing light. An enclosed
experimental apparatus equipped with a photodiode - or better still, a monochromator and a photomultiplier tube might answer this question.

*Are the Averaged Power Spectra regions valid?*

Again in Chapter Two, we divided the averaged power spectra into two distinct regions. It would be interesting to see if these regions are universal - i.e. that they can be applied to all CAE spectra.

*Periodicity*

In Chapter Three periodicity was observed in those experiments which did not produce regular oscillations. Are the oscillations indeed the result of dissolved oxygen release (as we suggest) or are they due to other physical or chemical processes?

*Is CO₂ gas evolved?*

Whether or not CO₂ gas is evolved is still argued in the literature. We attempted to answer this question through the use of a gas partitioner, but the rapid oscillations of the BR oscillator prevented reproducible results.

It is difficult to write possible CO₂ evolving reactions - the only source of carbon in the reaction mixture is the organic substrate, and it spends considerable time flipping into the enol form and abstracting I⁻ from iodine. Any side reaction which breaks down the substrate to produce CO₂ would have to compete with its iodide scavenging preference.
In 1987, Rubin and Noyes published measurements of critical supersaturation for homogeneous bubble nucleation\textsuperscript{63}. They discovered that the thresholds for the diatomic gases H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, CO and NO in aqueous solutions all lie between 0.012 and 0.07 M, while that for CO\textsubscript{2} was 0.4 M. Assuming that their measurements can be applied to the BR oscillator in at least a relative sense, then it may be that CO\textsubscript{2} never reaches the threshold required to give rise to significant bubble evolution.

\textit{Numerical Modeling}

In Chapter Five, we presented a modification to the BR oscillator’s skeleton mechanism and a rate for reaction D1 considerably lower than the currently accepted value. Unfortunately, there wasn’t sufficient time to test the validity of our model by numerical integration, and this is left for future researchers.
References

List of Manufacturers

(in alphabetical order)

AET Corporation Sacramento, California, USA
Alitea USA Medina, Washington, USA
BDH Chemicals Toronto, Ontario
Blue M Electric Co. Blue Island, Illinois, USA
Brüel & Kjær Naerum, Denmark
Campus Computers Vancouver, British Columbia
Cole Parmer Chicago, Illinois, USA
Fisher Scientific Nepean, Ontario
Hewlett Packard Richmond, British Columbia
IBM Corporation Boca Raton, Florida, USA
Ismatec Zurich, Switzerland
MacArthur Chemical Montreal, Quebec
Metrabyte Corporation Taunton, Massachusetts, USA
Nora Systems Vancouver, British Columbia
Orion Research Inc. Boston, Massachusetts, USA
Tektronix Beaverton, Oregon, USA
Proprietary Software Developed

The software listed here was developed in-house. Those programs marked with an asterisk were written by this author.

SIGNAL ACQUISITION

These programs acquire CAE signals from various digitizers and store them to disk in a proprietary file format designed by members of this research group. This format, “AES”, is a binary format designed for fast access and compact storage.

ACK* - supports Tektronix 2200 series digital storage oscilloscopes
ACQ2430A - supports Tektronix 2400 series digital storage oscilloscopes
ACQS2000 - supports Soltec SDA2000 digitizer
NOFRILLS* - supports Metrabyte PCIP oscilloscope adapter card

SIGNAL VALIDATION

Validation modules were written to check the performance of the digitizer hardware and software. They accept AES files as input and provide output to the screen or to flat ASCII files.

AESCHECK - flags under-triggered and over-ranged CAE signals
AESEEDIT* - graphical interface for deleting noise signals

SIGNAL ANALYSIS

The analysis programs accept AES files as input and provide interactive display and editing of CAE signals with the exception of TRAPS which is designed to run in an
automated mode. All programs generate flat ASCII files. TRAPS generates averaged power spectra files: AVP (entire experiment) or TRA (time resolved).

**AESEEDIT** - graphical interface for editing and manually classifying CAE signals

**AEVIEW** - graphical interface for inspection of all CAE data files

**TRAPS** - generates time-resolved averaged power spectra

**DESCRIPTOR EXTRACTION**

The main program is FEATURES which generates binary format descriptor (DS1) files from AES files. DS1EDIT accepts DS1 files for input and is especially useful for breaking down large data sets into smaller, more manageable, data files.

**FEATURES** - computes descriptors for CAE signals

**DS1EDIT** - interactive editing of descriptor files

**DESCRIPTOR ANALYSIS**

A variety of software has been written to aid in the analysis of the descriptor data once descriptors have been computed.

**AETREND** - calculates distributions and correlates with physical factors

**COMATRIX** - computes various measures of descriptor correlation

**DS1STATS** - generates univariate statistics for descriptors

**HCLUSTER** - performs hierarchical clustering

**K-MEANS** - performs non-hierarchical clustering

**PCA** - performs principle components analysis

**WILCOXON** - computes the Wilcoxon two-tailed rank sum test
OTHER SOFTWARE

PF*

This is the software written to perform the experiments detailed in Chapters Three and Four. PF was designed to operate and oversee all the instruments in use. For maximum flexibility, PF used both an “immediate” and a “script-based” system. In the immediate mode, the user could directly control any/all instruments. In the script mode, the user would write a simple, English language list of commands and store the list in a file. PF could then be instructed to read the file and process the commands in the list. This made repeated, unattended experiments possible.
CAE d.c (mV)
(decreasing left to right)

Figure C-1. Chart recording of Reagent Set A, Run 1 - oscillations present.
Figure C-2. Chart recording of Reagent Set A, Run 2 - oscillations present.
Figure C-3. Chart recording of Reagent Set B - no oscillations observed.
Figure C-4. Digitized chart recordings of Reagent Set A
Figure C-5. Data from series PF-G-1 and 2: [iodine] (top), CAE d.c. (middle dotted) and [iodide] (bottom).
Figure C-6. Data from series PF-G-3 and 4: [iodine] (top), CAE d.c. (middle dotted) and [iodide] (bottom).
Figure C-7. Data from series PF-G-5 and 6: [iodine] (top), CAE d.c. (middle dotted) and [iodide] (bottom).
Figure C-8. Data from series PF-G-7 and 8: [iodine] (top), CAE d.c. (middle dotted) and [iodide] (bottom).
Figure C-9. Data from series PF-G-9 and 10: [iodine] (top), CAE d.c. (middle dotted) and [iodide] (bottom).
Figure C-10. Data from series PF-K-1 and 2: [iodine] (top), CAE d.c. (bottom).
Figure C-11. Data from series PF-K-3 and 4: [iodine] (top), CAE d.c. (bottom).
Figure C-12. Data from series PF-K-5 and 6: [iodine] (top), CAE d.c. (bottom).
Figure C-13. Data from series PF-K-7 and 8: [iodine] (top), CAE d.c. (bottom).
Figure C-14. Data from series PF-K-9 and 10: [iodine] (top), CAE d.c. (bottom).
Figure C-15. Data from series PF-O-1 and 2: [iodine] (top), CAE d.c. (bottom).
Figure C-16. Data from series PF-O-3 and 4: [iodine] (top), CAE d.c. (bottom).
Figure C-17. Data from series PF-O-5 and 6: [iodine] (top), CAE d.c. (bottom).
Figure C-18. Data from series PF-O-7 and 8: [iodine] (top), CAE d.c. (bottom).
Figure C-19. Data from series PF-O-9 and 10: [iodine] (top), CAE d.c. (bottom).
Figure C-19. Data from series PF-T-1 and 2: [iodine] (top), CAE d.c. (bottom).
Figure C-20. Data from series PF-T-3 and 4: [iodine] (top), CAE d.c. (bottom).
Figure C-21. Data from series PF-T-5 and 6: [iodine] (top), CAE d.c. (bottom).
Figure C-22. Data from series PF-T-7 and 8: [iodine] (top), CAE d.c. (bottom).
Figure C-23. Data from series PF-T-9 and 10: [iodine] (top), CAE d.c. (bottom).
Figure C-24. Data from series PF-S-1 and 2: [iodine] (top), CAE d.c. (bottom).
Figure C-25. Data from series PF-S-3 and 4: [iodine] (top), CAE d.c. (bottom).
Figure C-26. Data from series PF-S-5 and 6: [iodine] (top), CAE d.c. (bottom).
Figure C-27. Data from series PF-S-7 and 8: [iodine] (top), CAE d.c. (bottom).
Figure C-28. Data from series PF-S-9 and 10: [iodine] (top), CAE d.c. (bottom).