Chapter 1. Introduction

1.1 Heat Conduction Calorimetry

The measurement of heat, defined as calorimetry, is of paramount importance in understanding chemical processes. Nearly all chemical, biological and physical processes involve heat thus rendering calorimetry as an indispensable thermodynamic tool to these disciplines (Brown, 1998; Calvet & Prat, 1963; Kemp, 1999). Different types and classifications of calorimeters have evolved in the efforts to measure the heat involved in a variety of processes and reactions. Three groups of criteria are used to classify calorimeters: (1) the principle of measurement, (2) the mode of operation, (3) and the type of construction (Hemminger & Sarge, 1998).

The Quartz Crystal Microbalance/Heat Conduction Calorimeter (QCM/HCC) as the name indicates is a form of heat conduction calorimetry. For the first classification criterion listed above, the principle of measurement in the QCM/HCC is defined as the heat-exchange principle. This method is characterized by the measuring of the temperature difference between the sample and surroundings. The method is based on the Tian-Calvet type calorimeter where the thermal events taking place in the reaction cell are permitted to flow freely to the surroundings, an aluminum heat sink in this case. The heat must first flow through thermal sensors; typically thermopiles are used for this purpose. The voltage potential produced by the thermopiles is proportional to the thermal power (Calvet & Prat, 1963; Wadsö, 1997).

The mode of operation, also described as the temperature conditions of the calorimeter, for the QCM/HCC can be classified as static. The temperature is not scanned but instead a constant temperature environment between the system and
surroundings is maintained. This categorizes the measurements as being isothermal. It is noted however that an ideally isothermal environment is difficult to establish. Temperature gradients occur when the heat flow to be measured first occurs in the reaction vessel. Thermal gradients can also occur because of undesired heat leaks in the construction of the calorimeter (Hemminger & Sarge, 1998).

The QCM/HCC was constructed following a twin or differential measuring principle. Identical sample and reference chamber are utilized and subject to the same conditions. The only difference between the two is that the sample chamber also contains the material being studied. The difference between the sample and reference chambers is monitored so that the measured heat effects are the result of the sample being studied (Giraldo & Moreno, 2000; Wadsö, 1997). Further details of the QCM/HCC construction and operation are given in Chapter 3.

1.2 Calorimetry in Education

One aspect of the research presented here involved a collaborative project to develop heat conduction calorimetry experiments that could be used in undergraduate physical chemistry courses. Analysts report that typically physical chemistry laboratories are unpopular in part due to the number of theoretical concepts that students must know prior to and during the experiments (von Nagy-Felsobuki, 1991). According to Piaget’s development of intelligence, when students approach a subject for the first time they are in the concrete operational stage of intellectual development. In order to intellectually operate at a formal level, students need relevant laboratory experiences (von Nagy-Felsobuki, 1991). On their first exposure to the concepts of thermodynamics, students cannot always see what is being measured (Crosby, 1988). This is where it is important
to have a curriculum that includes well-developed thermodynamic experiments in the laboratory.

Teaching physical chemistry may seem to be a daunting task in today’s world. Educators surmise that students find physical chemistry to be “too hard, too abstract, and worst of all, esoteric and irrelevant (Crosby, 1988; Schwenz & Moore, 1993).” Educators in the field of physical chemistry struggle to make the curriculum relevant to everyday experiences of physical chemistry. In any discipline, it is advantageous to step back, survey the current trends and techniques and to analyze whether the current educational process uses these current techniques and methods of analysis. According to a symposium sponsored by the American Chemical Society, there is a growing concern about the content of physical chemistry courses and laboratories. Because a relatively small number of students choose to take physical chemistry, updating instrumentation and the curriculum does not always get first precedence (Schwenz & Moore, 1993).

In planning a physical chemistry laboratory curriculum, there are many topics vying for attention that would benefit students, topics ranging from spectroscopic techniques, kinetics and computational studies. The area of thermodynamics is no exception and could use updating. Calorimetry has been a long-standing pillar in the determination of thermodynamic values such as heat capacity, specific heat and enthalpy changes. The isothermal heat conduction calorimeter described here has been utilized in the physical chemistry laboratories at Drexel University for the past six years. Students have had the opportunity to measure the heats from a variety of reactions and chemical processes. In addition, the students become acquainted with the inner workings of a calorimeter and
learn some aspects of concern in designing calorimeters. The calorimeter and its applications will be described in Chapter 2.

1.3 Quartz Crystal Microbalance/Heat Conduction Calorimetry

1.3.1 History of the QCM/HCC

The Quartz Crystal Microbalance/Heat Conduction Calorimeter (QCM/HCC) is a relatively new, unique instrument that allows simultaneous thermodynamic and rheological properties of thin films to be studied as a thin film is exposed to varying gas phase solvent activities.

The technique was created through the efforts of Dr. Allan Smith during a sabbatical at the University of Lund, Lund, Sweden. The technique was created to devise a method to measure the enthalpy of sublimation of solids with low vapor pressures at ambient pressures. Dr. Smith sought to develop a method that would simultaneously measure mass and thermal events. Coupling quartz crystal microbalance technology with existing heat conduction calorimetry brought this desire to realization.

The instrumentation has provided an avenue to probe sorption studies of thin films with a broad range of applications. Dr. Smith has continued in the development of this technology and has begun the construction of a second-generation instrument involving this technology.

1.3.2 Development of Instrumentation

Dr. Hamid Shirazi, a former Drexel graduate student, under the direction of Dr. Allan Smith, continued work in understanding the behavior of the instrumentation and its sensitivity (Shirazi, 2000). Hamid explored the use of an impedance analyzer to probe the behavior of the film-coated QCMs and also as a means of calibrating the
thermopiles. Many improvements were made in automating the instrumentation and data collection. Several LabView VI’s were written to control the operation and data collection of the QCM/HCC, mass flow controllers were added for the gas introduction, and several applications were explored ranging from polymer sorption, protein hydration, pharmaceutical measurements, to hydrogen sorption in palladium, and the formation of self-assembled monolayers (Smith & Shirazi, 2000; Smith et al., 2002). In conjunction, Mr. Jun Tian explored the use of the QCM/HCC in studying the organic vapor sorption behavior of C\textsubscript{60} films and C\textsubscript{60}-piperazine films (Tian, 2002).

1.4 Thesis Overview

Chapter 2 involves an educational aspect of calorimetry and the utilizing of a specially constructed “2-Drop” heat conduction calorimeter in the undergraduate physical chemistry laboratories. A brief survey of the current status of calorimetry in education is discussed. At Drexel University and in collaboration with Dr. Lars Wadsö of the University of Lund, Lund, Sweden and Dr. Thomas Hofelich of the Dow Chemical Company, Midland, MI, heat conduction calorimeters were designed and student experiments were explored. In addition to the original designs, Calorimetry Sciences Corporation, CSC, has manufactured a commercial 2-Drop Calorimeter. The company provided us with a commercial model to further explore its use as an educational tool. The basic design of the student calorimeters is discussed followed by a description of the calibration process and six experiments utilized by both the Drexel-built and the CSC 2-Drop Calorimeters.

Chapter 3 focuses on the Quartz Crystal Microbalance/Heat Conduction Calorimeter (QCM/HCC). A physical description of the instrumentation is given along
with an overview of the QCM/HCC experimental controls and data acquisition. A special word of gratitude is given to Mr. Jun Tian for the schematic diagrams of the QCM/HCC apparatus and setup. A few modifications and updating of equipment are also explained. The chapter is then dedicated to describing the mass and thermal sensing devices in the QCM/HCC, quartz crystal microbalances and thermopiles. Some background history and theory is outlined introducing quartz crystals and their use as microbalances. A portrayal of film-coated QCMs is given along with the equations describing their operation as mass sensing devices. Likewise, a general background is then given to explain the theory of thermopiles and their use as heat sensing devices. A description follows of the equations used to relate the voltage potential from the thermopiles to the thermal power resulting from the measured chemical processes.

Chapter 4 includes a survey of the thermodynamic and rheological properties that are accessible from the data analysis of QCM/HCC studies. The chapter is divided into three parts. The first section is devoted to the portrayal of sorption processes in thin films. Following this, a description of the thermodynamic analysis of the QCM/HCC data is given. Four avenues of data analysis are discussed in this section including the determination of sorption enthalpies, sorption isotherms, partition coefficients and diffusion coefficients. The final section of the chapter explains the rheological properties of thin films that are probed when using quartz crystal microbalances, namely the shear storage modulus, $G'$, and the shear loss modulus, $G''$.

Chapter 5 describes the application of the QCM/HCC in sorption studies of the cycloaliphatic poly(ether urethane) polymer, Tecoflex®. Several different film thicknesses ranging from 0.75 µm to 8.5 µm, were compared for their sorption of
ethanol and water vapor independently. This work was a collaborative effort comparing original studies with studies done by Dr. Hamid Shirazi, a former Drexel graduate student, and several undergraduate researchers including Jason Riggs, Rebecca Mason, Anna Ayrapetova and Betty Jacobs. Introductory background is given describing other polymer QCM studies and the properties of Tecoflex. The experimental parameters are outlined followed by graphs of the QCM/HCC data. The data is then analyzed and sorption enthalpies, isotherms, partition coefficients and diffusion coefficients are compared. Our attempts at analyzing the shear storage and shear loss moduli are described. Avenues that we explored in this area include DSC studies of Tecoflex, cold temperature QCM frequency measurements and the exploring of two methods known as the “Simple Three-Step Method” and the “Δf-ΔR” technique. The DSC studies were possible through the time and generosity of Dr. Andrew McGhie of the Laboratory for Research on the Structure of Matter (LRSM) at the University of Pennsylvania. The Simple Three-Step Method and Δf-ΔR techniques are the result of the comprehensive work on polymer coated QCMs by Dr. Ralf Luckum et al. On a recent visit to Drexel University, Dr. Ralf Lucklum of Otto-von-Guericke-University, Magdeburg, Germany, generously spent time in describing his studies and provided some helpful suggestions with our studies. He also provided us with a copy of an Excel spreadsheet, ZYSYN_QP.xls, which he devised and uses to model film-coated QCM responses.

Chapter 6 includes hydration studies of the proteins lysozyme and myoglobin using the QCM/HCC. The chapter begins with a general introduction of protein hydration studies. Prior work involving lysozyme hydration is described and a recent analysis of the diffusion coefficients is presented. The second part of the chapter deals with
hydration studies of the protein myoglobin. The parameters for the experiments are outlined and the initial data is presented in graphic form. A thermodynamic analysis of the sorption processes then follows. The chapter finishes with a sorption study of the buffer used in the myoglobin solution, sodium phosphate buffer. The effects of the buffer on the protein sorption studies are shown. A discussion of the possible hydrate formation of the buffer concludes the chapter.

Chapter 7 is a conclusion to the studies presented here. Some future experimental possibilities in the above-mentioned studies are described.
List of References


