Design of a Gas Sorption Measurement System

by

Scott Warren Davie

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Author

Department of Mechanical Engineering

May 17, 1991

Certified by

Nam P. Suh

Ralph E. and Eloise F. Cross Professor of Mechanical Engineering

Thesis Supervisor

Accepted by

Professor Peter Griffith

Chairman, Department Committee
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Abstract

In order to incorporate microcellular foaming in an industrial manufacturing process, the cycle time for foam generation must be minimized. To optimize the gas sorption process, quantitative data is needed to determine the coefficients of diffusion, solubility, and permeability of a polymer under varying saturation environments. These coefficients can be determined from a time history of the mass gain of the polymer. The goal of this project was to develop an apparatus to determine these properties by recording this mass gain. The operating parameters were up to 300°C and 3175 psi.

Two designs were considered: (1) a balance beam whose motion as the polymer sample sorbed gas would be recorded by an LVDT and (2) a pressure measurement system that would use a state equation to relate the pressure drop in an isolated chamber containing the polymer to the mass of gas it sorbed. Upon an examination of the relative difficulties of construction, robustness of performance under constant use, and ease of operation, the gas measurement device was chosen for further development.

This report introduces the microcellular foaming process and demonstrates the importance of the development of this apparatus in order to advance research in this area. A system design is then presented, and a summary of the practical and theoretical issues resolved during the design process is discussed. The report discusses the next steps to complete the construction of the device and finally summarizes the testing that must occur to establish its accuracy.

Thesis Supervisor: Nam P. Suh
Title: Ralph E. and Eloise F. Cross Professor of Mechanical Engineering
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Chapter 1

Introduction

The fundamental concept behind the creation of microcellular foamed plastic is based upon the sorption characteristics of polymers in gas environments. Comyn defines sorption as

...a generalized term used to describe the penetration and dispersal of penetrant molecules in a polymeric matrix to form a mixture. The sorption process can be described phenomenologically as the distribution of the penetrant between two or more phases to include adsorption, absorption, incorporation into micro-voids, cluster formation, solvation-shell formation and other modes of mixing.\(^1\)[7]

It is well known that plastics sorb solvents when subjected to an environment where these solvents are present in concentrations. Thus a polymer placed in a gaseous environment will gradually sorb the gas. This sorption process has two characteristic properties. The first is the diffusivity of the gas in the polymer; this property describes the rate at which the polymer will sorb gas, a strong function of the gas temperature and pressure in carbon dioxide systems. The second characteristic of the sorption process is the solubility of the gas in the polymer; also a strong function of the gas temperature and pressure, this characteristic determines the equilibrium quantity of gas that will be sorbed by the plastic. Thus increasing the pressure of the gaseous

\(^1\)Comyn, pg. 29
Figure 1-1: Process parameters input to the system determine the quality of the foam created.

environment results in a higher final concentration of gas in the polymer in a shorter span of time.

Once a polymer sample is saturated with gas, the next step towards foaming is to create a thermodynamic instability to spark the foaming process. Removing the sample from the gaseous environment and then, if necessary, heating it causes the void nucleation and growth needed for foaming to occur. By adding energy to the polymer-gas system the activation energy needed for nucleation is exceeded and the foaming of the polymer begins. The quality of the foam is determined by the number of nucleation sites and the size of the voids. The former determines the cell density. Void size is determined by the total amount of gas dissolved and the free expansion of the bubbles in the polymer. A microcellular structure requires void diameters of less than 10 $\mu$m. The difficulty of the foaming process lies in creating a dense, small, and consistent void structure throughout the material. Figure 1-1 shows a summary of the basic process parameters and the resultant properties determining the final foam quality.
Microcellular foamed plastics differ most basically from conventional foams in the size of their internal voids. Where as the voids of conventional foams range from several millimeters to several tenths of a millimeter in diameter, the voids of microcellular plastics fall well below 10 \( \mu m \) in diameter. Cell densities range between \( 10^9 \) and \( 10^{16} \) cells per cubic centimeter. Since these voids are smaller than original material flaws within polymers, they do not reduce the specific material properties and in many cases actually improve them. Impact strength, electrical insulation properties, and thermal insulation properties all may be improved by microcellular foaming. An advantage of microcellular plastics over conventional foams is the ability to make these improvements while reducing material consumption.

1.1 History of microcellular plastics

The first patent for microcellular plastic foam was filed in 1981 by Suh and Martini.[15] Martini completed the first experiments to develop a theoretical analysis of the formation and growth of voids in microcellular plastics.[16] For his Master of Science degree, Waldman developed foaming process parameters through an empirical analysis of the phenomena.[18] He examined mechanical properties and developed a design strategy for continuous and injection molding processes. Youn produced lightweight polyester composites in 1984 which led to approximately a 30% weight reduction over short fiber composites while increasing the specific strength and modulus of the polymer.[19] Colton and Suh in 1985 modeled the effect of various additives and processing parameters on the number of nucleation sites in foamed thermoplastics.[2] [3] [5] [6] [4] In 1988 Kumar modified a thermoforming process to develop a thermocycle for the manufacture of three dimensional microcellular foamed parts.[12] Finally just last year, Lempiainen completed a study of gas permeation through polymers[13]; Martini studied techniques to produce microcellular foamed fiber[14]; and Kim studied industrial applications for microcellular foamed materials.[11]
1.2 Present areas of research

Doctoral candidates are focusing research in three primary areas: supermicrocellular foam, extrusion of microcellularly foamed sheet, and injection molding of microcellular foam.

Supermicrocellular foam is the most recent advance in the foaming process. The tremendous advances made with this technique developed by Cha and Suh have produced foams with cell densities approaching $10^{16}$ cells per cubic centimeter on the order of 0.1 $\mu m$ in diameter. This dwarfs the 1-10 $\mu m$ cell size and concentration of $10^9$ cells/cm$^3$ typical of standard microcellular foams. In addition to the improvements in the structure of the foam, supermicrocellular foaming achieves all this in a small fraction of the time of the standard process.

The extrusion of microcellular foamed plastic is still very early in the development stages. Baldwin’s process consists of extruding the plastic into a saturation chamber where it travels a lengthy course to allow sufficient time for full saturation. It then leaves the saturation chamber via a dynamic pressure seal and enters a heated container where the foaming actually takes place. Finally the foamed sheet is collected on a spool.

Park is presently modifying an injection molding process to produce sequentially formed parts. Saturation of the polymer with gas during the process occurs near the end of the mixing screw where gas bubbles are injected into the polymer. As a result of the tremendous shearing process which the screw induces, the two phase bubble and plastic mixture rapidly become a single phase of saturated plastic. This plastic is then injected into a mold under pressure. Once the pressure drops as the mold is opened, cell nucleation occurs and foaming begins.
Chapter 2

Project Goal

At present the limiting factor in the production speed of microcellular foam is the saturation time necessary to ensure that sufficient quantity of gas has been sorbed by the polymer. Conventional microcellular foaming techniques require one to two days of saturation to achieve acceptable foam structure. Clearly this cycle time must be minimized to reduce manufacturing costs and make microcellular foam a viable production process. As discussed in the introduction, two primary characteristics define the sorption process: the diffusivity and solubility. By optimizing these characteristics, the quality of the foam can be improved while simultaneously reducing the saturation cycle time.

Up until the present time, reductions in saturation cycle time have come primarily through an iterative process. Little quantitative information is known about the precise state of the polymer during saturation and so a numerically based optimization of the process is thereby impossible. Obtaining a quantitative description of the saturation process clearly would prove a great benefit for all areas of research in this field. Knowledge of the sorption and diffusivity coefficients of polymers under different environmental conditions would give designers of both injection molding and extrusion processes a much better understanding of the physics of the processes and thus would improve their controllability. Thus a quantitative, time-dependent description of the state of the polymer throughout the saturation process is the goal of this research.
2.1 Theoretical foundation of the project

Through careful use of diffusion and solubility theories, knowledge of the mass gain of a polymer over time provides enough information to calculate relevant material constants. This section presents the basic conceptual approach to performing these calculations once the sample mass gain is known.

2.1.1 Determination of the coefficient of diffusion

In his book The Mathematics of Diffusion, J. Crank has assimilated much of the existing theory on diffusion.[8] He presents a number of models to describe the diffusion process. The model most applicable to this research is a plane sheet. The plane sheet model assumes a sample "...so thin that effectively all the diffusing substance enters through the plane faces and a negligible amount through the edges."\(^1\)

Several assumptions are made to further simplify the model: a constant diffusion coefficient throughout the saturation process; negligible swelling of the sheet; equal gas concentrations on both surfaces of the polymer sample; constant pressures and temperatures; and a negligible initial gas concentration in the sample. Then the mass of gas sorbed by a sample sheet suspended in a gaseous atmosphere can be measured. The assumptions permit the following solution to the relevant diffusion equation:

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left\{-D(2m+1)^2\pi^2 \frac{t}{l^2}\right\}
\]

where \(M_t\) is the total mass of gas sorbed by the sample at time \(t\), \(M_\infty\) is the equilibrium mass of gas sorbed by the sample at time infinity, \(D\) is the diffusion coefficient, and \(l\) is the thickness of the sheet. This derivation is based upon a model whose gas concentration at each surface immediately assumes its final equilibrium value upon becoming exposed to the gaseous atmosphere. The half-time of the sorption process,

\(^1\)Crank, pg. 44
Figure 2-1: The expected shape of a sorption curve relating mass gain to time for a polymer sample.

\[
\left(\frac{t}{l^2}\right)_\frac{1}{2}
\]

is that value of \(t/l^2\) when \(M_t/M_\infty = \frac{1}{2}\) and can be written as:

\[
\left(\frac{t}{l^2}\right)_\frac{1}{2} = -\frac{1}{\pi^2 D} \ln\left\{\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right\}
\]

(2.2)

\[
D = 0.409/\left(\frac{t}{l^2}\right)_\frac{1}{2}
\]

(2.3)

with an accuracy of 0.001 percent.²

Figure 2-1 shows the likely shape of a curve relating the mass gain of a sample to time. The equilibrium mass is easily identified as the asymptote that the mass curve approaches as time approaches infinity. \(M_{t=0}\) is the initial mass of the sample. The intermediary point between the two mass values occurs at the time when the mass gain is half the final mass gain of the sample. Correlating this point on the curve to the normalized time axis results in the sorption half time, \(\left(\frac{t}{l^2}\right)_\frac{1}{2}\). Inserting this value into equation 2.3 gives the diffusivity coefficient of the sample.

²Ibid, pg. 239
Figure 2-2: The expected shape of a plot of equilibrium concentrations for varying pressures.

2.1.2 Determination of the solubility coefficient

The solubility coefficient relates the equilibrium concentration of a gas in the polymer to the ambient gas pressure. This value can be empirically determined by plotting equilibrium gas concentrations versus gas pressure for a number of experimental trials as in Figure 2-2. Each data point is the result of a single experiment. According to Henry's law these points fit a line whose slope is the solubility coefficient $K_s$. Should the experimental data follow some other curve, different theories have been developed to derive $K_s$ from a higher order curve.[9]

2.1.3 Determination of the permeability coefficient

Once the solubility and diffusivity coefficients have been determined, the permeability coefficient $P$ is the result of a simple calculation. Assuming a constant diffusion coefficient and that the solubility coefficient is derived from a linear curve and not a polynomial:

$$P = DK_s$$

(2.4)
2.2 The goal of this project

The goal of this project is to design, build, and test an experimental apparatus to determine the mass of the gas sorbed by a polymer sample during up to a forty-eight hour period. The apparatus must accommodate different polymers and different gases at a constant pressure and temperature during each trial while allowing for changes in these parameters from one trial to the next. An automatic data acquisition system must record data at regular intervals during the trial.

The operating parameters of the system were defined by the Microcellular Plastics Consortium research group at the inception of this project. The system had to operate at a gas pressure up to 3000 p.s.i. and temperatures up to 300° C using both CO₂ and N₂ as processing fluids.
Chapter 3

The System Design

This design project began with the most basic functional requirement: determine the mass of gas sorbed by a polymer during a saturation period. Two possible approaches were investigated to fulfill this requirement. The first approach used a balance scale to directly measure the mass change of the polymer sample. The scale would deflect in direct proportion to the mass gain of the sample; this deflection would be detected by a linear velocity displacement transducer (LVDT). Thus the entire balance scale and LVDT system would be placed in a pressure vessel, and the LVDT electrical leads would pass through a seal in the wall of the chamber to an external data acquisition system.

The second design option was based upon the decrease in gas pressure which must occur as the polymer sorbs gas from an isolated high pressure environment. The increased mass of the sample occurs at the cost of a decrease in the mass of gas in the system. This change in thermodynamic state of the gas allows the calculation of the quantity of gas sorbed by the sample. Fig. 3-1 shows the complete design concept for this design approach.

Both approaches were investigated and further developed so that some comparison of the two could be made. A total system error was estimated for each case. The
Figure 3-1: The full system design for a pressure measurement apparatus to record the mass gain of a polymer sample.
The basic error equation for the pressure measurement approach is shown below:

\[ \epsilon^2_{\Delta M} = \sum_{m=1}^{N} \sqrt{\epsilon^2_N} \]  

(3.1)

This states that the error of measuring the change in mass of the polymer sample, \( \epsilon^2_{\Delta M} \), is the sum of all the error contributions of the \( N \) components of the respective system. Errors in the balance scale approach would be due to inaccuracies and tolerances in the LVDT, precisely measuring the geometry of the system, and determining the characteristics of a damper to stabilize motions of the balance. Error contributions of the pressure measurement system result from the temperature and pressure transducers, inaccuracies of volume measurements, inaccuracies of the state equation at higher temperatures and pressures, fluctuations in the boundary conditions, and errors from the data acquisition equipment. For both systems each error contribution was decomposed until as many possible sources of error were accounted for. The total system error in both cases was about 4% on the change in mass of the system. Therefore the two options could not be easily differentiated solely on the basis of system accuracy.

The research group then compared the two options on a variety of other levels. Both had several disadvantages. The balance scale approach was not very robust to environmental disturbances. This system would be rather delicate and subject to frequent breakdowns after prolonged exposure to the corrosive environment of high pressure, high temperature gas. The size of an entire balance beam and LVDT apparatus would require quite a sizable chamber.

The greatest disadvantage of the pressure measurement approach was its sensitivity to leakage in the system. After a forty-eight hour experiment even an extremely small leak in a tube or chamber seal would overwhelm the output signal, expected to be on the order of tens of p.s.i.. However, the research group concluded that the pressure measurement system most likely would be easier to construct and operate as well as more reliable. Thus, the majority of the group voted to pursue this option, and the detailed design of the apparatus began.
3.1 Functional requirements

The first step of the system design was to define the functional requirements that must be met to achieve the project goals. Figure 3-2 shows a tree of the basic functional requirements. As previously described the principal requirement of the system is to record a time history of the mass gain of a polymer sample subject to high pressure, high temperature, gas environment. The top layer of the tree states this project goal. The functional requirements of the next level reflect the need to measure all the state variables of the system in order to relate this decrease in pressure to a corresponding decrease in the mass of gas. The left side of the figure lists the actual state variables that must be determined to calculate the change in the mass of gas. The right side of the figure lists the requirements that must be satisfied in order to equate this change in gaseous mass to a change in sample mass—mainly the decrease in gas pressure must be accounted for solely by the increase in sample mass. Any leakage of gas to the atmosphere thereby will cause a significant error in the data. Likewise any pressure drop due to a decrease in temperature will similarly decrease the system accuracy.

3.2 Design requirements

The design parameters of Figure 3-3 represent physical requirements directly reflecting the functional requirements just discussed. Thus the left side of this diagram correlates with the left side of the functional requirement tree of Fig. 3-2. The volume of the system will remain constant. Thermocouples measure the gas temperature of the system. Pressure transducers determine the gas pressure of the system. The right side of the design parameter tree insures that pressure changes in the system are only a result of the polymer sorbing gas, a heating system controls the gas temperature, and leakage is prevented.
Functional Requirements of Weight Measurement System

Determine mass of gas absorbed by polymer over time

- Insure that pressure change of system is due solely to gas sorption of polymer
- Maintain constant volume of system
- Minimize effect of Sample volume

- Control energy input to system
- Minimize gas leakage

- Measure volume (V) of chamber
- Measure temp. (T) of gas
- Measure press. (P) as f(t)

Figure 3-2: A functional requirement tree for the experimental apparatus.
Design Parameters

Insure $\Delta P$ is due to gas absorbed by sample

Absorption chamber

Control temperature

Prevent leakage

All metal sealing

Band heaters

Heating system

Controllers

Fixed $V$ of reference chamber

Temperature transducer

Thermocouple

Differential

Absolute

Determine $\Delta P$ for a fixed volume chamber

Pressure transducer

Figure 3-3: A design parameter tree for the experimental apparatus.
3.3 The sample vessel

Although ensuring adequate strength of a pressure vessel is crucial, a critical aspect of the sample chamber design was the sealing of the vessel. This seal had to be virtually leakproof yet still allow relatively easy access to the chamber at the beginning and completion of each experiment. Implicit in this leakproof requirement was that no polymers could be used as part of the sealing system, i.e. no polymeric o-rings or gaskets could contact the gas. Several possible solutions to this problem were investigated. The first option investigated was a high tolerance metal v-ring manufactured by Parker Seals. This design depended upon a small amount of deflection of the metal to create a self sealing system under pressure. However this deflection requirement limited the life of the product to under 10 cycles. At a price of over $150 for a 3 inch metal ring, this approach appeared economically infeasible for a device that would be run hundreds of times.

The next sealing approach used a vacuum chamber product based on line contact between a hardened ridge and a replaceable soft metal ring. This system was designed to be self sealing in a vacuum system but, of course, was just the opposite in a pressurized chamber. That another student had little luck with this approach at low positive pressures quickly eliminated this from the options list.

Finally the possibility of designing and constructing a completely customized soft metal sealing system was examined. The sealing metal would be designed to deform under initial loading when first closing the vessel and then to deform further upon pressurization. The sealing surface would be designed and machined as part of the entire construction of the vessel. Each metal seal would deform completely upon usage so that a new one would be needed for every experimental test. This option appeared the most practical approach.

Once an adequate sealing system was designed for the sample chamber, the vessel itself would have to be constructed. Possible blind and weld flanges were identified as well as nominal pipe material. Stainless Pipe and Fitting Company in Cambridge estimated at least a month to acquire the needed material; due to the high pressure
Autoclave Seal Design

Figure 3-4: Detailed views of the sealing designs of two commercial chambers.

requirements of the system, it was highly unlikely that any mill would have such items in stock, and thus they would have to be specially produced. The estimated material cost for constructing the vessel was approximately $1100 dollars. In light of this initial cost before the considerable work and time was invested in order to develop an adequate sealing system, commercial options were investigated next.

The products of two different companies, Autoclave Engineering and Parr Instrument, were researched. The prices of the respective products were comparable, but the actual sealing design of each company was extremely different (see Figure 3-4). Parr’s seal relied on numerous contact points along a flat teflon ring to seal the chamber. David Rein, a chemical engineering doctoral candidate, has used a small chamber from this company and had great difficulty creating a precise seal; eventually he discovered the use of soft lead sheets in addition to the teflon as an effective solution. However his pressures of less than 200 p.s.i. was far below the requirements of the system under consideration, so effective sealing from a Parr product seemed impossible without significant post purchase modifications.

Fig. 3-4 shows how the Autoclave product used an entirely different seal design.
The diamond shaped seal ring is coated with a layer of silver to improve sealing along the contact surface. This design is self sealing; first the seal ring is initially loaded by tightening the flange bolts; then as the chamber is pressurized, this pressure pushes the seal ring outward and thereby increases the force the ring exerts upon the contact surface. Thus on the basis of sealing ability, the Autoclave product appeared to be far superior to that of Parr.

Finally a comparison was made between designing and constructing a vessel and sealing system versus buying an Autoclave vessel. The $1100 cost of a constructed vessel looked quite reasonable on paper, but behind this lurked an intensive investment of work and time in order to develop a precise, reliable, and easy to use sealing system. At best the integrity of the designed seal would probably be equivalent to the Autoclave system. That the designed seal would be inferior to the Autoclave system was even more likely. Thus the decision was made to buy a chamber with a seal that was already known to work well and thereby minimize the need for subsequent sealing alterations.

### 3.4 The pressure transducers

Beyond the sealing issues of the sample chamber, the specification of the pressure transducers for this system was the next most difficult, and most important, task. A decision early in the design process was made to use both an absolute and a differential pressure transducer. To obtain the necessary resolution at high pressures with a single transducer would be prohibitively expensive if not impossible. To ensure a sufficient resolution on the pressure change, a differential transducer could reference the sample chamber to another vessel devoid of any polymer. Therefore, an absolute pressure transducer would determine only the initial pressure of the system, and a differential pressure transducer would detect all subsequent changes in pressure.

Just as in the specification of the sample chamber, no polymers within the transducer should contact the process fluid of the system. This became an increasingly difficult and finally impossible criterion to uphold. All possible transducer options
contained some form of a polymer seal ring. Thus this criteria was adapted to become a need to minimize the amount of polymer in the transducer. For the transducer design finally chosen, polymer seal rings probably could be replaced with a metal seal should extensive leakage from the transducer become a source of system error.

The accuracy and resolution of the transducer was also an important selection consideration. Poor accuracy quickly eliminated the lowest performance transducers from consideration. The field of possible options eventually was narrowed to industrial and not laboratory specific designs. These industrial grade transducers normally are used to measure the flow rate of heavy process fluids by determining the pressure drop across a known orifice. The accuracy within this group all fell under one quarter of one percent.

The range of the transducer was of critical importance as well. Clearly measuring a change in pressure of ten p.s.i. with a transducer with a thirty p.s.i. range would be an inefficient use of the transducer. The desired transducer would have a maximum range equal to the largest expected pressure drop of the system. While appropriate calculations were made to determine the expected pressure drop (see chapter 4), two additional measures were taken to allow for some flexibility between the system pressure drop and the range of the differential pressure transducer. First a variable range transducer was specified. With the three to one turndown ratio of the Camille Bauer model, the full scale range could be reduced from 600 inches to 400 inches and finally down to 200 inches of H₂O. Thus when a sample is only expected to absorb a mass of gas equivalent to 5 p.s.i. the full scale range of the transducer could be reduced to 200 inches of H₂O in order to obtain maximum resolution.

However this turndown operation requires the use of a highly accurate pressure source with which to calibrate the transducer. So a second, more convenient approach to the problem was developed. The basis for the entire apparatus design requires that the pressure drop within the sample chamber be completely reflected by the change in mass of the sample. The gas pressure drops in proportion to \( \frac{\Delta M_{gas}}{\sum M_{gas}} \), the percentage change of the total gas mass in the chamber. Thus decreasing the total mass of gas in the chamber effectively amplifies the pressure drop resulting from a given mass sorbed.
by the sample. Therefore in order to increase the pressure drop of the system to make use of the full scale range of the transducer, the mass of gas in the system could be easily decreased by placing an inert dead volume in the chamber. It is important to note however that while this last method increases the effective resolution of the system it increases the error contribution due to any leakage in the same proportion. So the accuracy of the system is not necessarily improved.

The final criteria for the selection of the transducer was the format of the output signal. The analog to digital converter board already installed on the laboratory's Macintosh IIcx requires a voltage input signal to generate a digital output. Current output signals evidently are more commonly used than voltage output signals in industrial systems, and so not all transducers offered a voltage output format. Of course by sending a current through a resistor, a voltage drop could be measured across the resistor, but this would add noise and other errors to the signal and so was not preferable.

A last consideration in the design of the transducer system was the temperature operating limits on the device. The temperature limit of the transducer chosen is 250°F. Clearly it must be thermally insulated somehow from the much higher operating temperature of the pressure vessels. This thermal insulation is achieved by simply locating the transducer at the end of a length of tubing some distance away from the vessel. For every extra foot of tubing approximately a 100°F reduction in gas temperature can be expected. Thus locating the transducer three to four feet from the chambers should be adequate.

3.5 The heating system

A heating system design satisfies the functional requirement of maintaining the system at a constant temperature. The basic concept of the system as shown in Fig. 3-5 was to use the output signal of a thermocouple within each chamber to control the energy input into a heat source. The first design decision made regarding this system concerned the nature of this heat source. Two options seemed feasible: to immerse
Figure 3-5: A band heater, thermocouple, and temperature controller are the basic components of the heating system.
both chambers in a single liquid bath (probably of glycerine) or to use separate electrical band heaters directly in contact with the chamber. Operating safety, ease of use, and the controllability and accuracy of the system were the primary criteria used to differentiate the two options.

Clearly a heated and stirred liquid bath would provide more consistent heating. The high thermal inertia of the bath would reduce temperature oscillations and ensure that both sample and reference chambers would be maintained at precisely the same temperature. However this approach had serious disadvantages when compared to the other criteria. Completely submerging both chambers in hot liquid would definitely create quite a mess. At least part of this liquid would have to be drained off at the end of every trial to allow access to the sample chamber. While the thermal inertia of the liquid would provide easier controllability, it also would increase the cooling time necessary to access the sample chamber. A serious safety hazard could exist for the hurried operator who neglects to wait for the system to cool adequately or forgets to wipe the slippery glycerine off the lid of the chamber. An electrical band heater offers significant advantages for both the safety and convenience of the operator: no fumes from hot glycerine, no slippery parts to handle, and no need to add or drain hot fluid from anywhere. Of course the independent temperature controllers on each chamber increase the probability of a temperature difference between one and the other, but this deviation should be at most a few degrees. If it appears significant during testing, the liquid bath option could be pursued with relatively ease.

A low cost PID controller was chosen to control the electrical input to the band heater. This however is not a true PID design; the output is a non-continuous full-on or full-off type known as a bang bang controller. Thus the control law determines the duration of the input signal and not its magnitude.

Dual element E-type thermocouples were chosen for the temperature transducers. As shown in the design parameter tree of Fig. 3-3, thermocouples are necessary both to control the energy input to the system and to define the state of the gas in the system. Thus in each chamber the leads of one thermocouple are connected to the Analog Breakout Unit as part of the data acquisition system and the remaining set of

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leads is connected to the temperature control unit. An E-type junction was chosen for it's high operating temperature and low error qualities: up to 900°C with an error that is the greater of 1.7° C or 0.5%. Another critical parameter in the specification of the thermocouples of this system is the wall thickness of the device. The thermocouple must be sufficiently thick to provide a good sealing surface (see section 3.8).

3.6 The reference chamber

The functional requirement of the reference chamber was to safely contain process fluid up to 3000 p.s.i. at temperatures as high as 300°C. The high maximum operating temperature dictated the use of 316 stainless steel due to it's corrosion resistant properties and its low loss of strength at these conditions. The size of the vessel was really not critical as the interior pressure would not change. Since the chamber's only purpose was to provide a reference, access to its interior was not required. In fact it was not desirable as any access port is always a possible source of leakage. Thus the decision was made early on to weld the entire reference vessel shut regardless of the particulars of its construction. Both the height and the outer diameter of the chamber were designed to fit a specific band heater. The specification of the head and wall thickness was performed to ASME Pressure Vessel Code and is presented in chapter 4. Several different construction techniques were considered: machine all components and weld them; buy a tube and machine two flat heads from stock; buy a tube and endcaps, machine the desired openings, and weld them; or simply buy two endcaps and weld them directly together.

The last possibility initially appeared most attractive. On two stock end caps only a little drilling and tapping would be required for the gas and thermocouple ports and the two pieces could be quickly welded. However after some time spent trying to locate endcaps of the right material and thickness, it quickly became apparent that this approach would not be as simplistic as was tentatively hoped. The size of endcap required is quite uncommon, and thus no company stocks it as regular inventory. Instead they wait for a customer who needs these parts and then produce them in
quantity. Thus acquiring a single pair of endcaps would be both time consuming and expensive.

Buying all components and sending them to a welder also appeared relatively easy, yet suffered from the same problems as this approach did for the sample chamber: the end caps were quite expensive and very time consuming to obtain. This approach lead to the development of a third option: to buy stainless steel pipe and then machine endcaps. It definitely appeared the most feasible approach until attempting to locate the desired 316 stainless steel tubing. However, $2\frac{5}{8}$ round stainless steel for endcaps did exist in Cambridge. Thus a decision was made to use this round for the endcaps and bore out a third section of it for the chamber wall.

### 3.7 The valves and fittings

The design of the tubing layout for the system was akin to a geometry puzzle. However the valve system is one of the most critical features of this design and was no simple matter specify. A total of five valves are specified here (see Figure 3-6). The two gas supply valves off the second tee are used to isolate each chamber once they are filled with gas. The gas exits through these same valves and then back to atmosphere through the primary relief valve. Although this valve is designed as the primary gas release, each chamber has its own individual gas release valve as well. In the sample chamber an 1/8 inch tube is routed off the bottom of the chamber to provide a secondary gas release mechanism should the primary release valve become blocked by a sample or other foreign object. While the reference chamber has nothing in the interior to cause a blockage of the exit passage, a second gas relief allows gas to be blown through the chamber in order to remove any condensation that might collect there.

Choosing the best valve for use in this system proved nearly as difficult as specifying a pressure transducer. In order to prevent system leakage, polymer sealing rings in contact with the process fluid of the chamber were unacceptable. Presented with these requirements a vendor recommended either ball or plug valves. Subsequent
Figure 3-6: The valve system design.
examination of these options showed that they could not isolate any of the process fluid from polymer seals; also the plug valve could not tolerate any back pressure on the valve, i.e. the sample chamber alone could not be pressurized by leaving closed the gas source valve to the reference chamber. Although these two options were not satisfactory, the vendor was not able to offer any alternative.

Bypassing the vendor and contacting the valve company seemed the next necessary step if anything was to be accomplished. The representatives quickly demonstrated that the purpose of its vendor was field questions and act as a buffer so that it didn’t have to be bothered talking directly to its customers. However after cutting through the initial bureaucracy, another option finally was discovered. Needle valves are specified here to prevent contact between the process fluid of the chamber and polymer seals. On the downstream side of the valve, sealing is accomplished by metal to metal contact between the valve stem and a stainless steel seat (Fig. 3-7). On the upstream side of this seal, polymer o-rings are used to make a seal between the body and the handle of the valve. By orienting the valve so that gas enters the chamber by this side from the gas source, the gas of the chambers will only contact the metal to metal seal and isolation of the chamber gas from polymers is complete.

3.8 Sealing issues

Excellent sealing is the weak link in this design approach. At a 3000 p.s.i. chamber pressure, a 0.2% drop in pressure due to leakage would seem quite small. Yet this is equivalent to a 10 p.s.i. drop in pressure and would completely overwhelm the small change due to the sample sorption of the gas. Clearly the sealing of the system must be very good, but exactly how good cannot be known until the device has been constructed. Thus a number of contingency plans have been developed should they become necessary.

The sample chamber seal is the most critical and thus most suspect in the entire system. As previously described Autoclave marketed the best sealing design encountered, yet there was no guarantee that it would be sufficient. Since perfect sealing
Figure 3-7: The needle valve allows a polymer free sealing system.

Figure 3-8: Dimensioned view of Autoclave sealing area.
from the Autoclave design could not be counted upon, the possibility of a back-up seal was investigated. As shown in Fig. 3-8, the dimension on the vessel which determines the feasibility of a back up seal is the distance between the primary seal and the edge of the vessel. The back up seal could take the form of a silicon or metal o-ring or even a thin, soft metal sheet that would be replaced with each trial. The distance between the head and the flange ring of the vessel would have to be near zero when fully tight to compress a thin metal sheet to provide an effective seal. Also any groove machined into the flange for placement of an o-ring would mitigate the effectiveness of any metal sheet seal. A distance of 0.340 inches on the radius allows ample room for either option.

Another critical sealing point in the system occurs within the needle valves. Close examination of the design of this needle valve reveals one drawback to its implementation as a polymer free device, however. The needle valve is designed to be self sealing when the pressure of the upstream side exceeds the downstream pressure. As shown in Fig. 3-7 the process fluid produces a downward force on the valve stem that helps keep it seated. When gas pressure is applied from the other direction as specified in this design, the only force sealing the needle to the valve seat is derived from the force exerted on the valve handle, and thus the valve is not self sealing. To increase the integrity of the seal, it is therefore recommended that pressure be applied from the gas source during the entire duration of the experiment. This back-pressure could be as high as necessary to provide a good seal in the valve.

Another possible sealing difficulty may occur at the thermocouple compression fitting of each chamber. The manufacturer of these fittings claims that in order to obtain an effective seal, the wall thickness of the thermocouple must be greater than 0.028 inches. Any thinner wall may not allow the ferrule to coin out a sufficiently deep contact point in the thermocouple and therefore might not sufficiently seal the joint. Standard thermocouples should be tested in the system to determine if this is indeed the case. If leakage is a problem at this point, thermocouples should be ordered that have an extra thick wall thickness.

Several other techniques to improve the sealing of the system have already been
discussed. The welding of the reference chamber and the back pressure applied to the needle valve both are techniques to achieve this. This welding approach could be applied to other parts of the system as well if necessary. The entire tubing system could be welded together instead of using the present ferrule based fittings. Silver soldering could be employed as a less permanent alternative to a fully welded tubing system.

3.9 Experimental procedure

This suggested experimental procedure assumes that all testing has been completed and system operation is satisfactory. This procedure should be re-examined before implementation and a dry run of the system should be made. Clearly any changes and improvements in the system should be reflected in changes to this procedure.

1. weigh sample using precision scale in Tribology lab.

2. determine volume of sample.

3. turn on temperature controller for reference chamber and heat up.

4. blow gas through reference chamber to remove condensation.

5. turn off temperature controller for reference chamber to reduce risk of burns to operator.

6. remove bolts from sample chamber and carefully remove lid of chamber; remember that any damage to the seal or the sealing surface will likely prevent a good seal!

7. place sample in sample chamber.

8. carefully place lid of chamber back on and align bolt holes; remember that seal!

9. thread bolts into holes by hand and then tighten with wrench.
10. close all gas relief valves.

11. turn on sample chamber temperature controller.

12. set sample chamber temperature controller to desired temperature.

13. turn on reference chamber temperature controller.

14. set temperature controller on reference chamber to desired temperature.

15. take necessary measures to preheat gas source.

16. after chambers and gas source have reached desired temperature, open both gas entrance valves to the pressure vessels.

17. open valve from gas source.

18. once gas in chambers is fully equilibrated, close gas entrance valves on both chambers.

19. begin data acquisition.

20. check for new leaks in system.

21. wait for completion of experiment.

22. close gas source valve.

23. turn off heaters and wait for system to cool.

24. check that valve to gas source is closed.

25. open primary gas relief valve.

26. open gas entrance valves to both chambers.

27. if a problem in the primary gas release system occurs, open secondary gas relief valves.
28. **carefully** unbolCl head of sample chamber and remove lid of chamber; remember that seal.

29. remove sample.

30. **carefully** replace lid of chamber and align holes in flange; remember that seal.

31. tighten flange bolts at least finger tight to ensure seal ring doesn't get banged around.
Chapter 4

Theoretical Analysis

4.1 System Error

The critical numerical quantity to determine the accuracy of the data is the expected error of the system in determining the change in mass of the plastic sample. The compensated state equation,

\[ PV = zmRT, \]  

(4.1)

was used to relate the thermodynamic state of the gas to its mass \( m \). \( P, V \) and \( T \) are the the gas pressure, volume and temperature respectively. \( R \) is the universal gas constant, and \( z \) is the compressibility factor. To obtain this error value, each component of the state equation was decomposed into various error sources whose contribution to the overall system error was individually evaluated:

\[ \varepsilon_{\Delta M} = \sqrt{\varepsilon_{\Delta P}^2 + \varepsilon_{Vol}^2 + \varepsilon_{Temp}^2 + \varepsilon_{state\ equation}^2 + \varepsilon_{boundary\ conditions}^2}, \]  

(4.2)

4.1.1 Pressure component

Decomposing \( \varepsilon_{\Delta P} \) results in two sources of error: that due to the inaccuracies of the pressure transducer and that due to the subsequent electronic processing of the output signal. \( \varepsilon_{transducer} \) is given as the accuracy of the sensor and is 0.25% for the
device chosen. $\varepsilon_{\text{signal processing}}$ is given as 0.02

### 4.1.2 Volume component

$\varepsilon_{\text{vol}}$ can be decomposed into several different components. First is that due to the error in measuring the chamber and tubing volume. The measurement can be made using a hydrostatic test but will not account for any thermal expansion within the system. Another error exists from inaccuracies in the measurement of the sample volume which must be subtracted from the total system volume in order to obtain an accurate operating volume for each experiment. For small samples the volume displaced will be negligible, but for large samples this error contribution could be on the order of other system errors. The sample volume will likely be determined from basic measurements using calipers. However the error of this caliper measurement relative to the volume of the entire system is negligible and need not be considered.

Another error consideration was the volume error due to any expansion of the sample as it absorbs the gas.\(^1\) The basic diffusion theory presented in section 2.1 assumes that no swelling of the sample occurs; should it be determined that this is not a valid assumption, a more complex model must be derived. However the volume expansion during the saturation process is minimal, and its affects are further mitigated by using a chamber volume much greater than the sample volume.

### 4.1.3 Temperature component

The chosen E-type thermocouple specifies an error of 1.7° C or 0.5% whichever is greater. The thermocouple is connected to the DAC system on the Macintosh IIcx data acquisition system and so the errors of the two components are compounded. Thus in the worst case, errors on the temperature recorded for each chamber are a sum of the thermocouple error and the error of the data acquisition system. However deviations between the temperatures of the two chambers will affect the pressure

\(^1\)Note that this expansion occurs as the sample absorbs the gas and not as it foams subsequent to gas sorption.
difference between them. So temperature controller inaccuracies are another source of error.

4.1.4 State equation component

For the design system design process, a modified ideal gas law was used for the equation of state.[10] The $z$ factor incorporated in this equation is found from the reduced states of the system and is accurate to 4%. For actual data manipulation better state equations can be found to greatly reduce this error, (see chapter 5).

4.1.5 Boundary condition component

The error in the system due to deviations in the boundary conditions is not completely straightforward. Every experimental trial occurs at some nominal operating pressure, for instance at 800 p.s.i.. So the initial pressure of the system is 800 p.s.i.. The pressure then drops as the sample absorbs gas and this pressure drop is correlated to some mass gain of the sample. Clearly some restraints must be placed upon the size of this pressure drop. After a 200 p.s.i. drop the sorption characteristics of a polymer at 800 p.s.i. would no longer be modeled. However a one p.s.i. drop in pressure most likely would still be an accurate model of polymer sorption at 800 p.s.i.. The following discussion provides a mathematical basis for limiting this pressure drop sufficiently to model a system at a constant pressure.

The general equation of solubility relates volume concentration $C_v$ to the ambient gas pressure $P_{ambient}$ of the environment by the solubility coefficient $K_s$:

$$C_v = K_s P_{ambient}.$$  \hspace{1cm} (4.3)

To write the equation in terms of a mass concentration $C_m$ a unit conversion factor $K$ is needed:

$$C_m = K K_s P_{ambient}.$$  \hspace{1cm} (4.4)
The above terms \( C_m, K \) and \( K_s \) can be written according to their definitions:

\[
C_m = \frac{m_{\text{gas in sample}}}{m_{\text{sample}}} \tag{4.5}
\]

\[
K = \frac{\rho_{\text{gas (STP)}}}{\rho_{\text{sample}}} \tag{4.6}
\]

\[
K_s = \frac{V_{\text{gas (STP)}}}{V_s \times \text{psi}}.\tag{4.7}
\]

Now differentiating the mass concentration definition of equation 4.4 results in:

\[
\Delta C = KK_s \Delta P_{\text{ambient}}. \tag{4.8}
\]

Rewriting equation 4.4 to solve for \( K_s \) and then substituting the definition of \( C_m \) into the equation results in:

\[
K_s = \frac{C_m}{K \times P_{\text{ambient}}} = \frac{1}{K \times P_{\text{ambient}}} \times \frac{m_{\text{gas in sample}}}{m_{\text{sample}}}. \tag{4.9}
\]

which can be substituted back into the preceding equation 4.8 to obtain:

\[
\Delta C = \frac{\Delta P_{\text{ambient}}}{P_{\text{ambient}}} \times \frac{m_{\text{gas in sample}}}{m_{\text{sample}}}. \tag{4.10}
\]

Differentiating the definition of the mass concentration results in:

\[
\Delta C = \Delta \left( \frac{m_{\text{gas in sample}}}{m_{\text{sample}}} \right) = \frac{\Delta m_{\text{gas in sample}}}{m_{\text{sample}}}. \tag{4.11}
\]

Now equating this differential with that obtained in equation 4.10 results in:

\[
\frac{\Delta m_{\text{gas in sample}}}{m_{\text{sample}}} = \frac{\Delta P_{\text{ambient}}}{P_{\text{ambient}}} \times \frac{m_{\text{gas in sample}}}{m_{\text{sample}}} \tag{4.12}
\]

\[
\frac{\Delta m_{\text{gas in sample}}}{m_{\text{gas in sample}}} = \frac{\Delta P_{\text{ambient}}}{P_{\text{ambient}}}. \tag{4.13}
\]

This \((\Delta m_g)/m_g\) is actually a percentage. Using the knowledge developed in the functional requirement tree that \( m_{\text{gas in sample}} = \Delta m_{\text{sample}} \) provides the overall system
error component:

\[
\frac{\Delta m_{\text{gas in sample}}}{m_{\text{gas in sample}}} = \frac{\Delta(\Delta m_{\text{sample}})}{\Delta m_{\text{gas in sample}}} \quad (4.14)
\]

\[
= \frac{\Delta C_m}{C_m} = \epsilon_{\text{variation in boundary layer}} \quad (4.15)
\]

which was the original goal of this derivation.

### 4.2 Reference chamber calculations

The material thicknesses used for design of the reference chamber shown in Figure 4-1 were calculated from equations given in Division 1 of Section VIII of the Rules for Construction of Pressure Vessels of the ASME Boiler and Pressure Vessel Code.[1] The code is written for vessels with a diameter greater than the proposed design; yet Allen Roby, the ASME representative responsible for this section of the code, stated that this requirement existed for some obscure legal protection and that all the equations of the section can be applied to a vessel of a smaller diameter.

The basic equations to determine the wall thickness of a vessel under internal pressure are given in code UG-27:

\[
t = \frac{PR}{SE - 0.6P} \quad (4.16)
\]

determines the circumferential stress in the chamber wall and

\[
t = \frac{PR}{2SE + 0.4P} \quad (4.17)
\]

determines the longitudinal stress. \( P \) is the maximum pressure in the chamber, 3175 p.s.i.. \( R \) is the inside radius of the chamber and is 0.875 inches for this design. \( S \) is the maximum allowable stress value of the material given by Subsection C of this section; for the 316 stainless steel bar used at 650° F \( S \) is 12,300 p.s.i..[2] \( E \) is the joint efficiency of welded joints; from Table UW-12 of the code, a non-radiographed butt-weld has a

---

[2] ASME Boiler and Pressure Vessel Code, pg. 403
Figure 4-1: A dimensioned drawing of the reference chamber as built.
joint efficiency of 0.6.\textsuperscript{3} The greater required thickness between the longitudinal and circumferential stress equations is the minimum allowable thickness of the chamber wall. For this particular design the circumferential thickness is greater, and so the minimum thickness is 0.265 inches.

UG-34 details the necessary equations to determine the thickness of flat heads of a vessel. For a circular flat head that is not attached by bolts the relevant equation is:

$$t = d\sqrt{CP/SE}$$  \hspace{1cm} (4.18)

where $P$, $S$, and $E$ are those used in UG-27, $d$ is the inner diameter of the chamber-1.75 inches for this design, and $C$ is a dimensionless factor dependent upon the particular method of attaching the head to the shell. For the general type of weld specified, a worst case value of 0.33 was used for the calculation.\textsuperscript{4} This resulted in a minimum head thickness of 0.659 inches.

Further calculations must be made beyond those of UG-27 and UG-34 to ensure that the head is adequately thick to allow for access ports for thermocouples and gas input and relief. UG-36 describes the parameters regarding openings in pressure vessels. The most relevant section of this code is UG-36-c-2 and UG-36-c-3. The former states, “All openings shall be reinforced to satisfy the requirements of UG-37, except as given in (3) below.” Part (3) then continues: “Single openings in vessels not subject to rapid fluctuations in pressure do not require reinforcement other than that inherent in the construction under the follow conditions: ...threaded...connections in which the hole cut in the shell or head is not greater than 2 3/8 in. diameter.”

Thus to invoke the exception of UG-36-c-3 there must exist a single opening less than 2 3/8 inches in diameter that is not subject to rapid pressure fluctuations. Since the inner diameter of the vessel being designed is less than 2 3/8 inches, this criteria is immediately brought into question. This numerical qualification clearly has been established for the larger diameter vessels that the code has been written for. Since it is not known what the maximum hole size is that does not require reinforcement,

\textsuperscript{3}ibid, pg. 105.2
\textsuperscript{4}ibid, pg. 37
invoking this exception cannot be justified and thus the requirements of UG-37 must be satisfied.

UG-37 immediately refers to section UG-39 for the reinforcements required for openings in flat heads. Part d of this section dictates that for openings with a diameter less than half the head diameter, using the lesser of 2C or 0.50 in equation 4.18 will give an adequately reinforced head thickness. For the system under discussion, the required thickness is then 0.812 inches. An additional safety factor was added on top of this to bring the head thickness to an even 1.00 inches.
Chapter 5

The Next Steps Towards Final Assembly

Hopefully this thesis will provide all the information necessary for the next research student to continue the project immediately from where it has been left off. This section provides the researcher with the next tasks that need to be accomplished in order to make the system fully operational.

All parts for the system have been ordered and delivered except for material for the stand and the two thermocouples. Dual element thermocouples should not be ordered before testing is performed with thermocouples of a standard wall thickness to determine if this type can be used. A relay on one of the new temperature controllers is not functional, and so this must be sent back to the manufacturer. An absolute pressure transducer should be found from a source within the Laboratory for Manufacturing and Productivity.

A frame must be designed and built to hold the pressure vessels and transducers. This should allow all the components to placed on one of the tables in the laboratory. The stand must: support the two vessels and the transducers, insulate the vessels to minimize energy loss, allow easy access to the sample chamber and valve system,

A small but important component of the system is a sample holder to keep the polymer from resting on the floor of the chamber. This need not be a complicated component. It simply must permit gas exposure to all surfaces of the sample. Placing
the sample on a coarse mesh or suspending it within the chamber are two possible solutions to this problem.

The data acquisition system must be set up to accept the output of the various transducers. Transducer leads can be connected to the analog breakout unit. Then some simple software must be written to record the output of the temperature and pressure transducers. The sampling time of the analog to digital converter can be very high relative to the rate of change of the system, and so a relatively continuous time history of the system will be obtained. Since only four states must be accounted for, the programming will not be particularly complex. From the values of temperature and pressure, the mass gain of the sample could be calculated and displayed every sampling period.

Finally a more accurate state equation would greatly improve the accuracy of the numerical processing of the transducer outputs. The National Institute of Standards would prove a good starting point for tracking this information down for both CO₂ and N₂ gasses. This may take the form of an accurate value for compressibility factors throughout the operating pressures and temperatures or instead be an entire state equation that fits the gas behavior by using numerous terms.
Chapter 6

The Final Tests

Once the device has been fully constructed, a number of tests must be performed on the completed system in order to ensure its accurate operation. Testing for system leakage will be the most critical of these. Pressurizing the system without any sample will allow the user to observe pressure drops in the system due to imperfect sealing. Sizable leaks can be easily detected using a liquid detection fluid that will form bubbles at leakage points. If the system is still leaking after these have been stopped, more involved tests must be performed. Individual components of the system could be tested individually to isolate the problem area. Then the most likely causes identified in section 3.8 should be examined first and the recommended approaches considered.

A test that must be performed is a volume measurement of the system. This is best accomplished by determining the volume of water that the system can hold. Known volumes of water should be added to the system until all areas of it are filled. This may require breaking the seals in some of the piping in order to allow air to bleed off and ensure all areas of the piping are fully filled with water.

Another test run should check the maximum temperature experienced by the differential pressure transducer at it’s off site location. Placing an extra thermocouple at the junction where the transducer is connected will make this an easy measurement to make. This thermocouple could replace the pressure transducer for the testing period or could become a permanent fixture of the system if desired. Should the temperature at this site exceed the rated operating temperature of the transducer, the
Figure 6-1: Expected sample masses that will result in a 10 p.s.i. pressure drop for different operating parameters and different maximum mass gains of the sample.

length of tube isolating the transducer from the heated chambers could be increased or could pass through a bath of water to remain cool.

To maintain the accuracy of the system, the temperature controllers must keep both the sample chamber and reference chamber at the same temperature. The output of the two pressure transducers should be compared to ensure that the controllers are accomplishing their task. If manipulation of the controller gains cannot ensure this requirement, than the heating fluid approach may have to be incorporated to the system.

Fig. 6-1 provides an initial starting point for experimental operation. These relations establish a 10 p.s.i. drop in pressure for the various polymer and operating characteristics. The relation is based upon the basic state equation 4.1 which in differential form can be written as

\[ \Delta P = \frac{zR}{V} mT. \]  \hspace{1cm} (6.1)

This graph is only meant as a reference tool to help establish an area of operating
parameters. Obviously if this exact information were available already, the entire project would be unnecessary.
Bibliography


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