REDESIGN OF AN ISOCHORIC APPARATUS FOR *P-V-T* STUDIES

A Senior Honors Thesis

by

JARED JON JOHANSEN

Submitted to the Office of Honors Programs
& Academic Scholarships
Texas A&M University
In partial fulfillment of the requirements of the

UNIVERSITY UNDERGRADUATE
RESEARCH FELLOWS

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Group: Physical Sciences

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Approved as to style and content by:

James C. Holste	Kenneth R. Hall	Edward A. Funkhouser
(Fellows Advisor)	(Fellows Advisor)	(Executive Director)

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ABSTRACT

Redesign of an Isochoric Apparatus for *P-V-T* Studies. (April 2001)

Jared Jon Johansen
Department of Chemical Engineering
Texas A&M University

Fellows Advisors: Dr. James C. Holste
Dr. Kenneth R. Hall
Department of Chemical Engineering

Industry and academia require accurate Pressure – Volume – Temperature (*P-V-T*) relationship data for various mixtures. Equation of state (an equation which models P-V-T relationships) development requires such data. A new equation of state is under development by National Institute of Standards and Technology (NIST) and more *P-V-T* data are necessary for its completion. Texas A&M has supplied such data in the past; however, the apparatus used for obtaining this data requires modernization. The new design incorporates automation and a new method for making pressure measurements. The new device consists of an isochoric (constant volume) cell, a pressure transducer, a platinum resistance thermometer, various insulation systems, and an automated control system. The new design can operate at temperatures ranging from 200K to 600K and pressures from full vacuum to 35 MPa, and has been designed primarily for work with natural gas mixtures.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Thermodynamics is an old science that still plays an important role in modern science and engineering. The laws of thermodynamics govern all matter. Knowledge of the laws of thermodynamics and thermodynamic properties is useful for design of anything from an internal combustion engine to a computer chip.

Equations of state (EOS) have been developed that predict the phase behavior of different substances based upon a set of parameters specific to each mixture or specific to each of the components of a mixture. Such equations are very useful because they allow prediction of great quantities of information based upon relatively little data. Van der Waals developed the first EOS of consequence in 1873 based upon the hard sphere model of gases. Commercial software packages such as Aspen and Hysis use equations of state extensively for modeling chemical processes.

Cubic equations of state enjoy wide use because of the accuracy they provide with little computational complexity. Additionally, such equations require only a few (three or four) substance specific parameters, most of which are readily available. Examples of such parameters include critical temperature and critical pressure.

Equations of state allow prediction of many thermodynamic properties from vapor pressure to Helmholtz energy, but are normally stated in the form of pressure as a

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This thesis follows the style and format of the *AIChE Journal*

function of temperature and density. The Redlich Kwong equation is an example of one such equation (Abbot, 1996):

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)} \qquad (1)$$

More complicated equations of state exist, requiring more terms and more parameters. The additional accuracy available from these equations makes them worth their computational complexity in some situations. Currently the National Institute of Standards and Technology (NIST) is developing an equation of state for natural gas mixtures, however more *P-V-T* (Pressure-Volume-Temperature) data are necessary for its completion.

In the past *P-V-T* data were collected at Texas A&M using a semi-automated isochoric apparatus in addition to several other devices. This device was constructed and operated as part of the dissertation work of Yurttaş, under the direction of Holste and Hall. The original goal was for the device to be fully automated, however this proved difficult, and a semi-automated design was implemented (Yurttaş, 1994). An alternative design has been proposed and some early feasibility calculations performed by Matabe indicated that the device could be redesigned in such a way that it could be fully automated without an appreciable affect on the accuracy of the instrument (Matabe, 1999). This work details the design of a new apparatus designed for natural gas mixtures.

CHAPTER II

THEORY

Laboratories throughout the world employ many methods for making *P-V-T* measurements, including isochoric, isobaric and isothermal methods. An isochoric method was selected for this work because it is a convenient method from an experimental point of view. At Texas A&M other devices including a densimeter and a Burnett apparatus are used in addition to the isochoric apparatus to capitalize on the strengths of each device and to cross-check data.

An isochoric device is a device that measures changes in pressure and temperature of a given system without changing the density or specific volume of the system. This is accomplished through the use of a sample cell that does not change volume or allow mass to escape or enter over the course of an experiment. Experimentally this is impossible; however, efforts can be made to reduce both mass transfer and volume changes substantially.

Phase Change Detection

The isochoric device's chief strength is its ability to accurately detect phase changes. Since most of the work performed in this field involves a wide range of temperatures and pressures, apparatus construction prevents visual detection of phase changes. For example most apparatus are constructed of opaque materials such as stainless steel and not transparent materials such as glass. Additionally the isochoric apparatus allows for more accurate measurements of changes in enthalpy than other devices.

Phase changes are accompanied by a discontinuous change in the slope of an isochore. As shown in Figure 1, an isochore is a constant density path on a phase diagram. By plotting many isochores the complete phase boundary of a given system can be determined. In Figure 1 the phase boundary is the curved line passing through the isochores at sharp changes in isochore slope. Liquids exist in the upper left portion of the graph and vapors exist at the bottom right portion of the graph. Liquid and vapor exist in equilibrium in the region contained by the curved phase boundary line. The upper right portion of the graph is the super critical region in which neither vapor nor liquid exist, but rather a supercritical fluid exists. This region makes possible transformations from liquid to gas without an observable phase change.

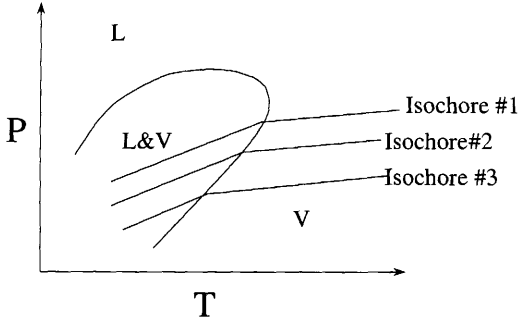

Figure 1 – Phase Diagram for a Mixture

Enthalpy Changes

Enthalpy changes can be derived from isochoric *P-V-T* measurements by making use of several thermodynamic relations (Abbot, 1996):

$$\Delta U = \int \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \qquad (2)$$

The quantity $\left(\frac{\partial P}{\partial T}\right)_v$ is the change in pressure with respect to temperature at constant volume, which is also the slope of an isochore. Therefore, by determining the slope of experimentally determined isochores, changes in internal energy, ΔU, may be derived. This equation shows the strength of the isochoric apparatus. An isochoric apparatus measures isochore slopes almost directly, while other apparatus require more calculations, and therefore introduce more uncertainty into the calculation of changes in internal energy. The change in entropy, ΔS, can be evaluated with a similar equation:

$$\Delta S = \int \left(\frac{\partial P}{\partial T}\right)_V dV \qquad (3)$$

After determining changes in internal energy and entropy, the other energy functions can readily be determined by making use of the following relationships:

$$\Delta H = \Delta U + \Delta(PV) \qquad (4)$$

$$\Delta A = \Delta U - T\Delta S \qquad (5)$$

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

Equation 4 is used to calculate the quantity of interest, ΔH, the change in enthalpy. Gibbs free energy, G, and Helmholtz free energy, A, are used less commonly in practice.

CHAPTER III

APPARATUS

An isochoric device has four basic needs: a constant volume cell, a temperature measuring device, a pressure measuring device and a control system. All four elements are necessary to insure proper operation of an experiment and to obtain meaningful data.

Isochoric Cell

The first element of the design, the constant volume cell, is responsible for insuring that the behavior of the cell is truly isochoric. All materials are subject to changes in volume with changes in temperature; however, some materials are less affected by temperature than others. Therefore, materials with low coefficients of thermal expansion are desirable for sample cell construction. Additionally the sample cell must also contain samples over a wide range of temperatures and pressures (up to 34.5 MPa or 5000 psia for this apparatus), requiring a material with high tensile strength. Also the cell must have a high thermal conductivity and low heat capacity, so the temperature of the cell can be changed quickly when moving from point to point while mapping an isochore. A high strength to weight ration is useful for minimizing time required to move between measurements, because the thermal mass of the cell can be minimized by reducing the total mass of the cell as well. The cell must also be chemically inert. If the sample cell material reacts with the sample, or catalyzes a reaction, then the sample composition will change, and quite possibly the mechanical integrity of the cell will be damaged.

For this work natural gas mixtures are of concern, which often contain hydrogen sulfide, H_2S, which corrodes many metals. In order to overcome this reaction, 316 stainless steel was chosen as the material of construction. Stainless steel is strong and has a reasonably low coefficient of thermal expansion; however, it has a low thermal conductivity compared to metals like aluminum and copper. This low thermal conductivity results in slower measurements; however, stainless steel was deemed a reasonable compromise for satisfying the criteria outlined above.

Isochoric behavior includes more than just restricting changes in volume, changes the quantity of mass in the cell must also be restricted. This is accomplished by minimizing locations for leaks to occur. The cell has only two openings and one main seal. Previously delta-ring seals and c-ring seals have been employed to insure mass did not escape the cell (Duarte, 1988) (Lau, 1986). However this apparatus employs the use of a seal manufactured by Garlock Helicoflex, a subsidiary of B. F. Goodrich. The Helicoflex seal is a reverse C-ring which contains a spring specifically chosen for the operating conditions of the seal (see Figure 2).

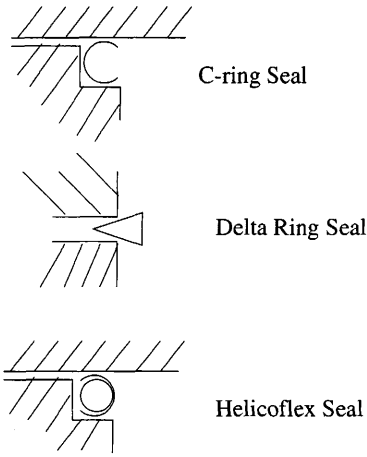

Figure 2 – Ring Seal Cross-Sections

The Helicoflex seal required a high seating force (5000 N per cm of circumference), resulting in the need for a thick flange and large bolts. In order to determine the optimum configuration (number of bolts and flange thicknesses), Calculations were performed according to the ASME Boiler and Pressure Vessel Code, Division 1, Section VIII, Appendix Y. These equations were manipulated using a Microsoft Excel spreadsheet to minimize the volume of metal in the flange and bolting materials (See Appendix B). Eight 5/8" by 2.5" long bolts made of B8M Material were selected. B8M material is 316 stainless steel and was selected because of concerns

regarding differential thermal expansion of bolts and cell material during operation of the apparatus. In some cases such differential thermal expansion has led to joint failure.

The geometry of the vessel was determined by the ASME Boiler and Pressure Vessel Code, using the thick-walled vessel formulas (See Appendix A). The resulting vessel has an operating range from (-75°C to 300°C and full vacuum to 34.5 MPa). The vessel is cylindrically shaped in order to bring the fluid to equilibrium faster (see Figure 3). The thermal conductivity within the metallic cell wall is higher than the thermal conductivity of the fluids to be examined by this apparatus. As a result, decreasing the average distance between a molecule of sample and the cell wall causes heat transfer to occur more rapidly. Additionally a cylinder allows for a small seal. A sphere would minimize the volume of metal necessary to contain the fluid; however, it would require a large seal along a great circle of the sphere because of construction limitations.

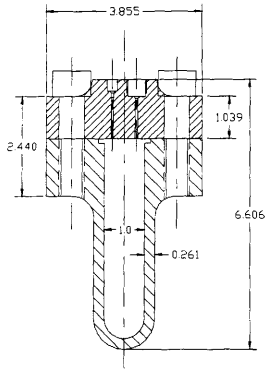

Figure 3 – Sample Cell Cross-Section

Temperature Measurement

The second element of the isochoric apparatus is a temperature measuring device. This apparatus makes use of a platinum resistance thermometer. This four lead device is connected to a computer operating National Instruments' Lab View software, for the purpose of recording and controlling the experiment. The sample cell is embedded within a large copper block to dampen temperature gradients within the cell and to aid in bringing the cell to thermal equilibrium faster. The sample cell and copper block must also be insulated to insure that the temperature measurement is meaningful.

Heat transfer is accomplished by four main mechanisms: conduction, convection, mass transfer, and radiation. Mass transfer has already been addressed by efforts to insure that the device is truly isochoric. Insulating the sample cell in a high quality vacuum (10^{-4} Torr) nearly eliminates heat transfer by conduction and convection. Two vacuum pumps in series produce and maintain this vacuum. The first pump is a mechanical pump capable of relatively high capacity but capable of only a moderate vacuum. The second pump is a diffusion pump with low capacity, but capable of producing a high vacuum. These two pumps operate in tandem to insure satisfactory insulation of the cell.

Placing a radiation shield around the cell curbs the fourth form of heat transfer, radiation. The radiation shield consists of a piece of metal maintained at a temperature about half a kelvin below the temperature of the sample cell. This temperature is maintained by circulating cooling fluid through tubes in the shield and by heating the shield with electrical wires.

To obtain meaningful data, the sample cell must be monitored to be sure that it is in equilibrium before taking measurements. This is accomplished by placing three thermocouples in different locations about the sample cell and measuring the temperature differences between the thermocouples. When all of the thermocouples indicate there is no temperature gradient within the cell, then a measurement may be taken and recorded.

Pressure Measurement

The third item necessary for an isochoric apparatus is a pressure measuring device. In the past, reliable high accuracy measurements have been made using pressure transducers produced by TTI, which measured quartz crystal capacitance changes as a function of pressure, nearly independent of temperature. Presently these devices are no longer available, forcing the design of new isochoric apparatus to measure sample pressure by a new method.

Paroscientific manufactures the most accurate and precise pressure transducer on the market today. The Paroscientific device measures changes in the natural frequency of a quartz crystal as a function of pressure. Unfortunately this device is highly temperature dependent and must be recalibrated every time its temperature changes. As a result it is desirable to maintain this pressure transducer at a constant temperature through out the experiment.

To measure the pressure of the sample, the pressure transducer must have contact with the sample fluid by some direct or indirect manner. In the past a metallic diaphragm was inserted between the sample fluid and another fluid which entered the pressure transducer. This method was successful in producing reliable data, however the process of determining the equilibrium pressure at a particular point was manual and iterative. Automation schemes for this procedure were examined, however most schemes were not considered sufficiently reliable nor safe enough to leave the device operating unattended for extended periods of time.

The new method for making pressure measurements involves a "noxious volume" contained within the pressure transducer and the tubing and fittings connecting the pressure transducer to the cell. This noxious volume is open to the sample cell and filled with the sample substance; however, it is not in thermal equilibrium with the sample cell. The noxious volume is at the same temperature as the pressure transducer and at the same pressure as the sample cell.

According to calculations performed by Matabe, so long as the noxious volume represents less than 1% of the cell volume, then the error introduced by the noxious volume has less impact on the accuracy and precision of the measurements than the thermal expansion of the cell (Matabe, 1999).

To thermally isolate the pressure transducer from the sample cell, the thin line connecting the two is made of stainless steel (relatively low thermal conductivity), with the thinnest wall thickness applicable to the pressure range of the vessel (see Figure 4). Additionally the pressure transducer is mounted in a block of copper maintained at a single temperature by thermoelectric cooling. A thermocouple mounted in this copper block and connected to the computer control system will insure that the pressure transducer is at the proper temperature before taking a measurement.

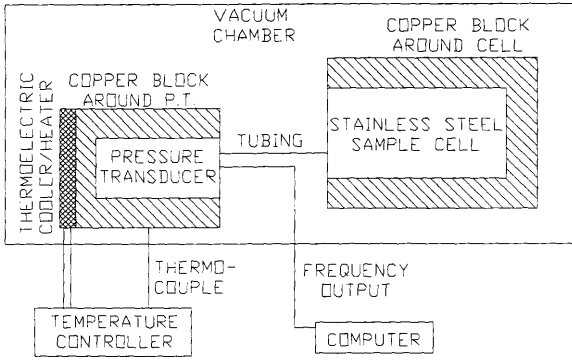

Figure 4 – Pressure Measurement System

Control System

Automation of the apparatus is accomplished through the use of a computer running National Instruments' Lab View software. This software is used in conjunction with hardware to record measurements for an isochore and to move from point to point along an isochore (see Figure 5). By monitoring and controlling the temperature of the sample cell, the software is able to move from point to point along an isochore.

Before taking measurements, the software first checks for equilibrium. Equilibrium is insured by checking for temperature differences between thermocouples mounted at various points on the sample cell and on the radiation shield. Additionally

sample cell pressure is monitored to determine if equilibrium has been achieved. Finally the temperature of the pressure transducer is monitored to insure that it has not deviated from the temperature at which the transducer was calibrated.

After equilibrium criteria have been satisfied the software records the temperature and pressure of the sample and then moves on to the next data point by either heating or cooling the cell.

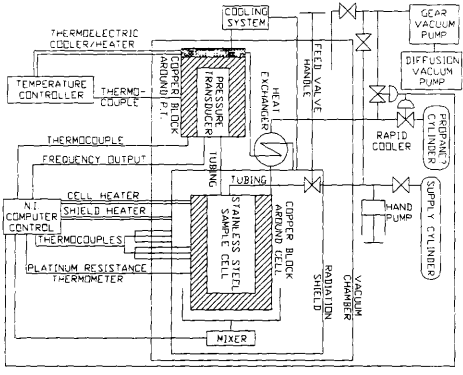

Figure 5 – Overall Apparatus Schematic

CHAPTER IV

CONCLUSION

The design outlined in this paper has the capability of making fast isochoric measurements with little or no supervision over the course of an isochore. Even moving between isochores might be automated in the future with automated valves. This apparatus is capable of measurements with precision and accuracy competitive with the best isochoric devices in the world today.

Cylindrical vessels are better for an isochoric apparatus because they reduce the required mass of material, reduce the sealing surface, and come to equilibrium faster because of better heat transfer characteristics. Greater degrees of accuracy and precision require greater degrees of complexity in the experimental apparatus. For instance – decent pressure measurements require an independent system for maintaining a constant temperature for the pressure transducer, independent of the sample temperature.

Overall the design seems satisfactory; however, the true test of this will come after completion of apparatus construction.

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APPENDIX A

VESSEL WALL THICKNESS CALCULATIONS

Based on ASME Boiler and Pressure Vessel Code Section VIII, Division 1, Appendix 1 additional design formulas, (1-1) Thick Wall Cylindrical Shells.

Terms

E = Joint efficiency = 1 (no welds)
S = Maximum allowable stress at operating conditions = 12,600 psi @ 600°F
P = Design pressure = 5000 psi
R = Internal radius = 0.500 inches
R_G = Ring groove outer radius = 0.650
t = Shell thickness

Main Shell

Longitudinal Stress

Z = P/(SE) + 1 = (5000 psi) /(12600 psi) + 1 = 1.39683

$t = R\,(Z^{1/2} - 1) = 0.500 \text{ inches} * (1.397^{1/2} - 1) = 0.092$ inches

Circumferential Stress

Z = (SE + P) / (SE – P) = (12600 psi + 5000psi) / (12600 psi – 5000 psi) = 2.31579

$t = R\,(Z^{1/2} - 1) = 0.500 \text{ inches} * (2.316^{1/2} - 1) = 0.260885$ inches

Required Wall Thickness = 0.26 inches

Flange Ring Groove Region

Longitudinal Stress

Z = P/(SE) + 1 = (5000 psi) /(12600 psi) + 1 = 1.39683

$t = R_G\,(Z^{1/2} - 1) = 0.650 \text{ inches} * (1.397^{1/2} - 1) = 0.139226$ inches

Circumferential Stress

Z = (SE + P) / (SE – P) = (12600 psi + 5000psi) / (12600 psi – 5000 psi) = 2.31579

$t = R_G\,(Z^{1/2} - 1) = 0.650 \text{ inches} * (2.316^{1/2} - 1) = 0.339152$ inches

Required Wall Thickness at Ring Groove= 0.34 inches

APPENDIX B

FLANGE MINIMIZATION SPREADSHEET

Symbol	value	units	parameter / explanation	Required condition	value	left	right
A	3.855	in	Flange OD	$S_b < S_a$	TRUE	20496.06	22000
C	2.605	in	Bolt Circle Diameter	$S_a < 1.5*S_f$	TRUE	5896.329	16800
B_1	1	in	Vessel ID	$S_a < S_f$	TRUE	12600	12600
G	1.163	in	Gasket/Seal effective diameter	$S_f < S_f$	TRUE	10331.5	12600
g_0	0.28	in	wall thickness at flange neck	$(S_a + S_b)/2 < S_f$	TRUE	9249.665	12600
g_1	0.28	in	wall thickness at flange neck	$(S_a + S_b)/2 < S_f$	TRUE	9115.417	12600
P	5000	psi	Design Pressure	$S_{bp} < S_b$	TRUE	12236.84	12600
n	8		Number of bolts				
d_b	0.625	in	Nominal Bolt diameter				
A_m	0.202	in^2	Minor bolt area				
D	0.836	in	Diameter of bolt hole				
H_G	10884	lb	gasket load due to seating pressure plus plus axial force generated by self-seating gasket				
t_f	1.401	in	thickness of vessel side flange				
t_g	1.039	in	thickness of blind flange				
S_f	12600	psi	Maximum allowable stress in flange material at operating temperature				
S_b	22000	psi	Maximum allowable stress in bolt material at operating temperature				
f_s	1		factor for integral type flanges from Figure 2-7.6 in ASME BPV Code, Section VIII, Div 1, Appendix 2				
F	0.90892		factor for integral type flanges from Figure 2-7.2 in ASME BPV Code, Section VIII, Div 1, Appendix 2				
V	0.550103		factor for integral type flanges from Figure 2-7.3 in ASME BPV Code, Section VIII, Div 1, Appendix 2				
bolt spacing	0.398	in					
Flange volume	27.4	in^3					
A_b	1.616	in^2	Total cross sectional area of bolts				
a	2.56349206		shape factor				
AR	0.62073463		bolt hole aspect ratio				
B_1	1.26	in	mid wall diameter				
C_1	0.11530993		factor				
C_2	-6341.73975		factor				
C_3	0.01808998		factor				
C_4	-1045.856		factor				
E	25300000	psi	modulus of elasticity of austinitic stainless steel at 600F				
E_f'	69510620.3	lb/in	factor				
E_g'	26374804	lb/in	factor				
$E_f'\theta_{MT}$	6971.73028	lb/in-rad					
$E_g'\theta_{MT}$	2645.88019	lb/in-rad					
$E_f'\theta_{MP}$	7297.48306	lb/in-rad					
$E_g'\theta_{MP}$	9121.9468	lb/in-rad					
F_i'	0.21909652		Flange factor for category 1, class 3 assembly				
H	5311.52604	lb	Total hydrostatic end force				
H_D	13924.5412	lb	contact force between mating flanges				
H_D	3926.99082	lb	hydrostatic end force for flange interior				
H_T	1384.53523	lb	difference between H and H_D				
h_D	0.50990195	in	factor				
h_G	0.625	in	distance from bolt circle to Flange OD				
h_D	0.6725	in	distance from bolt circle to mid-wall				
h_T	0.76175	in	distance from bolt circle to location of Force H_T				
h_G	0.721	in	distance from bolt circle to seal diameter				
J_g	1.41267617		factor				
J_p	1.08468135		factor				
K	3.855		Ratio of Flange OD to ID				
l	1.25147001	in	calculated strain length of bolt	used $l_b = t_g/2$ instead of $l_b = t_g + d_b/2$ because one end is threaded			
M_g	13705.9023	in-lb	moment due to H_D, H_T, H_G				
M_{dt}	-919.737739	in-lb	total moment on flange ring due to continuity of hub, pipe, or shell				
M_{dt}	-6869.8996	in-lb	total moment on flange ring due to continuity of hub, pipe, or shell				
M_{ut}	4063.3263	in-lb	unbalanced moment acting at diameter B_1 of flange				
M_{ub}	-1666.93546	in-lb	unbalanced moment acting at diameter B_1 of flange				
MD_t	-5003.06404	in-lb	balanced moment acting at diameter B_1 of flange				
MD_b	-5003.06404	in-lb	balanced moment acting at diameter B_1 of flange				
R	0.5425	in	distance from bolt circle to vessel OD				
r_B	0.16653593		bolthole flexibility factor				

VITA

Jared J. Johansen was born on June 28, 1977 in Beaumont, Texas. He is the olde of two children of Marie L. De Chatelaine and Jonathan E. Johansen. In May of 1996 Jared graduated from William Howard Taft High School in San Antonio. After entering the chemical engineering program at Texas A&M, Jared worked for both Huntsman Petrochemical Corp. and for Fluor Daniel. In May of 2001 Jared expects to receive a B.S. in Chemical Engineering from Texas A&M University.