Thermodynamic studies of polymers under high pressure.

Ludwig G. Khoubesserian
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THERMODYNAMIC STUDIES OF
POLYMERS UNDER HIGH PRESSURE

BY
LUDWIG G. KHOUBESSERIAN

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at
University of Windsor

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ABSTRACT

From a study of pressure-volume-temperature data taken from 25°C to 95°C and up to 23 kilobars, a high pressure equation of state and some thermodynamic quantities were obtained for polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polyvinylchloride, polycarbonate resin ("Lexan"), acetal resin ("Delrin"), Nylon 6, Nylon 610, Nylon 66, polytetrafluoroethylene ("Teflon"), fluorinated ethylene-propylene copolymer ("FEP", "Teflon 100").
ACKNOWLEDGEMENTS

I would like to extend my thanks and appreciation to Dr. R. A. Stager for his able guidance in all phases of this project.

Thanks are also extended to Mr. R. Proby and Mr. H. Parlar for their help in the construction of the experimental equipment and high pressure cell.

Finally I would like to thank the National Research Council for their financial support of this project.
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CHAPTER I
INTRODUCTION

The state of high pressure technology as is known today can largely be credited to the work of P. W. Bridgman.

Bridgman investigated the effect of pressure and temperature on physical properties of a great number of materials ranging from pure metals to polymers. While the pressures reached in his preliminary work did not exceed ten kilobars (see Appendix A for pressure units), with improvement of techniques and the introduction of high strength materials such as cobalt cemented tungsten carbide, he was able to obtain pressures in excess of one hundred kilobars.

Recent work done in the high pressure field includes research on simulated geological reaction kinetics, synthesis of materials such as industrial diamonds, study of phase diagrams and transition points, and investigations of the degradation and physical property behaviour of polymers.

In this thesis high pressure compressibility measurements were used to develop an equation of state for several commonly used plastics.
CHAPTER II

LITERATURE REVIEW

The first attempt made to study the behavior of polymers under high pressure was conducted P. W. Bridgman (1). He investigated the compression of thirty eight polymeric materials up to 40 kilobars at room temperatures. No special care was taken in choosing samples and the data obtained were not treated in any way. The value of this paper lies in its qualitative introduction of high pressure work to the plastics field and in its interpretation of the results obtained from the compression of "Teflon" (polytetrafluoroethylene). Bridgman noticed a transition point for "Teflon" at approximately six kilobars at room temperature. Since then this transition point has been verified by a number of researchers and found to be in the neighbourhood of five kilobars.

Rigby and Bunn (2) were the first investigators to study temperature effect on the properties of "Teflon" at atmospheric pressure. They observed a phase transition at eighteen degrees centigrade. X-ray studies showed that this transition was due to the rearrangement of the "Teflon" molecule.
Furukawa, McCosky and King (3) studied the phase transition in "Teflon" by observing the associated latent heat. Prompted by the behaviour of "Teflon" a number of investigators proceeded to study the behaviour of other semi-crystalline polymers.

Basic research was done by Richards (4) and Sperati, Franta and Starkweather (5). They related the crystallinity of polyethylene to its density and observed the effect of both molecular weight and molecular weight distribution on crystallinity. For this work x-ray and infrared techniques were used. Starkweather, Moore, Hansen, Roder and Brooks (6) did similar work on nylons. To this date only "Teflon" has displayed a pressure induced transition.

A number of investigators including Larsen and Drickamer (7) have studied the mechanical degradation and cross linking of polymers by plastic deformation at high pressures. It is interesting to note that of all the plastics studied, those having unsaturated olefinic or aromatic bonds produced an insoluble gel, whereas saturated polymers only degraded.

Weir (8,9,10) investigated the effect of temperature and pressure on volume for a number of polymeric
materials. He proposed a phase diagram for "Teflon" and derived an equation of state for some polymers by fitting his data to a linear polynomial of the third order in pressure and second order in temperature. The applicable range of Weir's equation is two thousand to ten thousand kilograms per square centimeter and twenty to eighty degrees centigrade.
CHAPTER III

THEORY

It is always desirable to adopt a theoretical approach in deriving an equation of state for a system. For a gas, perfect disorder or randomness of the atoms can be assumed. In the case of a solid, perfect order is assumed. Deviations of real gases or solids from these theories are then accounted for by applying the necessary corrections to the theoretical equations. In the case of polymeric materials relatively successful attempts have been made in formulating mechanical models describing some of their physical properties. However since the molecular structure of polymers is partly crystalline and partly amorphous it has not been possible, so far, to obtain a satisfactory mathematical model from which an equation of state can be derived.

It should be emphasized that "crystallinity" when referred to polymers does not have its conventional meaning. The crystals are regions of high order within the polymer. In order to understand further the meaning of crystallinity in polymers it is appropriate to give some attention to the form taken by the crystalline regions and to the manner in which they grow (11).
The development of crystallization in a high polymer depends strongly on two factors: the ambient temperature and degree of deformation. A specimen heated above its normal crystalline melting temperature may crystallize under the application of stress as does natural rubber (polyisoprene). On the other hand the same specimen may be cooled so rapidly that the mobility of the molecules is reduced greatly before they can rearrange into an orderly or "crystalline" array, and thus the material may exist in a completely amorphous form at a temperature well below its "freezing point". The optimum conditions for crystallization are obtained when the temperature and the deformation are such that the molecules have sufficient energy and mobility to associate in an ordered way but not sufficient to dissociate under the influence of random thermal motion. In the undeformed state there is generally a temperature different for each polymer, at which crystallization takes place most rapidly. For cis-polyisoprene this temperature is -25°C, where crystallization is virtually complete in about eight hours (12).

The experimental conditions determine not only the rate of crystallization but also the morphology.
of the crystalline structure. Perfect single crystals have been grown from dilute solutions of linear polymers and possess well defined crystallographic shapes. In undeformed solid polymers, however, semi-crystalline masses ("spherulites") are generally observed, growing outwards from separate nuclei until their boundaries meet thereby stopping the process.

When crystallization is induced by stretching in a polymer yet another crystalline morphology is encountered. It consists of a fibrous structure oriented in the direction of the applied stress. For polyisoprene this phenomenon occurs at high extensions (300% or over).

A transition between spherulitic and fibrillar crystallization occurs as strain is gradually superimposed upon thermal treatment of the specimens. Electron diffraction of thin films indicate that this transition is associated with an abrupt change in the orientation of the crystalline regions; in spherulites the molecular axis is perpendicular to the film, but with fibrillar crystallization it lies in the plane of the film (13).
Calculation of thermodynamic quantities in terms of experimentally measurable quantities.

The equation of state derived in this thesis is of the form

\[ V = f(T, P) \]  

(1)

Compressibility and dilation are defined as

\[ K = \frac{-\delta V}{\delta P} \] \hspace{1cm} \[ \alpha = \frac{\delta V}{\delta T} \]  

(2) (3)

Work of compression can be written as

\[ W = \int P \, dV \]

where

\[ dV = \left( \frac{\delta V}{\delta T} \right)_P \, dT + \left( \frac{\delta V}{\delta P} \right)_T \, dP \]

when at constant temperature we have

\[ W = \int P \left( \frac{\delta V}{\delta P} \right)_T \, dP \]  

(4)

Heat of compression is defined as

\[ Q = \int T \, dS \]

where

\[ dS = \left( \frac{\delta S}{\delta P} \right)_T \, dP + \left( \frac{\delta S}{\delta T} \right)_P \, dT \]

from Maxwell's relationship, we have

\[ (- \frac{\delta S}{\delta P})_T = \left( \frac{\delta V}{\delta T} \right)_P \]

therefore the expression for isothermal heat of compression becomes

\[ Q = -T \int \left( \frac{\delta V}{\delta T} \right)_P \, dP \]  

(5)
Using equations (4) and (5) we can calculate changes in internal energy during compression

$$\Delta E = Q - W$$ \hspace{1cm} (6)

and the change of entropy during compression

$$\Delta S = \frac{Q}{T}$$ \hspace{1cm} (7)

Heat capacity is defined as

$$C_v = \left( \frac{\partial Q}{\partial T} \right)_v = \left( \frac{\partial E}{\partial T} \right)_v$$

$$C_p = \left( \frac{\partial Q}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p$$

At constant pressure, the change in the heat quantity can be written as

$$dQ = dE + d(PV) = dH$$

therefore

$$\left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial Q}{\partial T} \right)_p$$

but

$$\left( \frac{\partial Q}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

therefore we can write

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

then the change of $C_p$ with respect to pressure can be obtained

$$\left( \frac{\partial C_p}{\partial p} \right)_T = T \left[ \frac{\partial}{\partial p} \left( \frac{\partial S}{\partial T} \right)_p \right]_T$$

$$= T \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial p} \right)_T \right]_p$$

using Maxwell's relationships, we have

$$(- \frac{\partial S}{\partial p})_T = (\frac{\partial V}{\partial T})_p$$

therefore

$$\left( \frac{\partial C_p}{\partial p} \right)_T = -T \left[ \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial p} \right)_T \right]_p$$

$$= -T \left( \frac{\partial V}{\partial T} \right)_p$$ \hspace{1cm} (8)
The change in entropy for a system can be written as
\[ dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT \]
differentiating with respect to temperature, we have
\[ \left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + \left( \frac{\partial S}{\partial T} \right)_V \]
but
\[ C_P = T \left( \frac{\partial S}{\partial T} \right)_P \]
and
\[ C_V = T \left( \frac{\partial S}{\partial T} \right)_V \]
therefore
\[ \frac{C_P}{T} = \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + \frac{C_V}{T} \]
from Maxwell's relationships, we have
\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]
therefore
\[ C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \]
Now let us write the expression for the change in pressure
\[ dP = \left( \frac{\partial P}{\partial T} \right)_V dT + \left( \frac{\partial P}{\partial V} \right)_T dV \]
differentiating this with respect to temperature, we obtain
\[ \left( \frac{\partial P}{\partial T} \right)_P = \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial T}{\partial T} \right)_P + \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]
therefore rearranging we have
\[ \left( \frac{\partial P}{\partial T} \right)_V = - \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T \]
therefore
\[ C_P - C_V = - T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T \]
\[ = - T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T \]
\[ (9) \]
CHAPTER IV

EXPERIMENTAL APPARATUS

The apparatus used in this experiment is shown in Figures 1, 2 and 3. It consisted of a 200 ton Rodgers hydraulic ram (model Cl-8A-8) in combination with a Blackhawk "ener-pac" hand pump (model P-39). The oil pressure was measured with a 10" Heisse Bourdon gauge (0-3000 psi range, 5 psi graduations). The relative displacement of the ram piston (Figure 4) was measured with a Mercer dial indicator gauge (0-0.5" range, 0.0001" graduation). A constant temperature oil bath regulated by a Winsco thermoregulator (±1°C) was used whenever needed.

The high pressure cell (Figures 3 and 4) consisted of two 0.25" diameter "Carboloy" (cemented tungsten carbide) pistons fitting into a hollow "Carboloy" cylinder (see Appendix B for specifications of "Carboloy"). Both the pistons and the cylinder were reinforced by steel rings (see Appendix C for construction of cell).

In order to prevent sample leakage between the pistons and the cylinder wall gaskets were placed at either end of the sample (Figures 3 and 4). These were
0.006" thick and 0.248" in diameter and were cut from soft steel stock.
FIGURE 1. EXPERIMENTAL APPARATUS

FIGURE 2. RAM AND PRESS FRAME
FIGURE 4. SCHEMATIC VIEW OF THE HIGH PRESSURE CELL
CHAPTER V

EXPERIMENTAL PROCEDURE

A. Cell Calibration for Pressure

The cell in this experiment was calibrated by observing the compression of certain materials having known first order phase transitions at high pressures. Table 1 shows the materials used for calibration and Figure 5 shows the calibration curve obtained.

<table>
<thead>
<tr>
<th>Compound or Element</th>
<th>Transition Pressure (kbars)</th>
<th>Volume Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td>2.3</td>
<td>-</td>
</tr>
<tr>
<td>KBr</td>
<td>18.0</td>
<td>-10.5</td>
</tr>
<tr>
<td>KCl</td>
<td>20.2</td>
<td>-11.0</td>
</tr>
<tr>
<td>Bi I-II</td>
<td>25.3</td>
<td>-5.0</td>
</tr>
<tr>
<td>Bi II-III</td>
<td>26.8</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

B. Blank Calibration for Displacement

The displacement data obtained by the experimental method was the total of the compressions of the plastic being investigated, the gaskets, the pistons, the "Carboloy"
FIGURE 5. CALIBRATION CURVE

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plates and insulating block. In order to obtain the compression of the plastic samples a blank run was made using the cell assembly as shown in Figure 4, without the plastic sample. Displacement data obtained in this manner at different temperatures were then subtracted from the corresponding experimental runs and data representing true polymer compression were obtained.

C. Sample Preparation

All the polymeric materials were machined to 0.246" diameter and 0.2 to 0.3 inches from rods. The calibration materials were obtained in powder form. The powders were placed in the cell and compressed into pellets which were used in the calibration of the cell.

D. Run Procedure

Before a run was started, the cell and pistons were cleaned and a set of new gaskets were prepared. A cylindrically shaped plastic sample was placed in the cell and the cell was assembled as shown in Figure 3. The cell was immersed in a constant temperature bath and this system in turn was placed between the main pistons of the press as shown in Figure 4. The temperature was set and at least thirty minutes were allowed to let the system come to thermal equilibrium. At each temperature setting a
maximum pressure of 24 kbars was applied to the system two or three times, in order to form the gasket seal between the cell pistons and the wall. Then the experimental readings were taken in the following manner:

Relative linear displacement of the cell pistons was recorded at each pressure setting until a maximum pressure of 22.6 kbars was obtained in the cell. The pressure was then released and a second run was made on the same sample. In all cases both sets of measurements agreed quite well and it was not necessary to perform any additional runs. There was no observed hysteresis effect. The above procedure was repeated at 10 centigrade degree intervals, from 25°C to 95°C.
CHAPTER VI

DATA REDUCTION

A. Pressure-Volume Correlation

As the first step in evaluating the experimental results, the blank displacement corrected data was treated to find a linear relationship between displacement and pressure. A run was chosen at random and a number of plots were made between several functions of displacement \( l \) and pressure \( P \). A very satisfactory straight line relationship was found to exist between displacement and the natural logarithm of pressure. In order to check the validity of such a relationship for all the runs, the correlation factor for each run was calculated (14), with results indicating that a relationship of the form

\[
1 = n + m \times \ln P
\]

(10)

would be valid to at least the 99% confidence level.

B. Temperature-Pressure-Volume Correlation

For each plastic sample tested, two runs were made at each temperature, therefore for every temperature setting two values of each \( n \) and \( m \) were obtained from equation (10). The arithmetic average values of each \( n \) and \( m \), namely \( \bar{n} \) and \( \bar{m} \) for every test temperature was
used in obtaining simple $\bar{n}$-temperature and $\bar{m}$-temperature relationships. Correlation factor calculations indicated that equations of the form

$$\bar{n} = A' + B' \times T_c$$

and

$$\bar{m} = C' + D' \times T_c$$

are acceptable at the 95% confidence level, where $T_c$ is temperature in degree centigrade.

C. Equation of State

Substituting equation (11) in (10) we obtain

$$1 = A' + B' \times T_c + (C' + D' \times T_c) \times \ln P$$

if we assume standard conditions to be 20°C and 1 bar; then equation (12) becomes

$$l_0 = A' + B' \times 20 + (C' + D' \times 20) \times \ln .001$$

where $l_0$ represents the length of the sample at the standard conditions and is measurable. Subtracting (13) from (12) we have

$$\Delta l = B' \times (T_c - 20) + (C' + D' \times T_c) \times \ln P$$

$$- (C' + D' \times 20) \times \ln .001$$

Since the diameter of the cell is constant during the experiment then

$$\frac{\Pi r^2 \Delta l}{\Pi r^2 l_0} = -\frac{\Delta V}{V_0} = \frac{-\Delta l}{l_0}$$

Therefore dividing equation (14) by $l_0$ and using
equation (15) we obtain

\[-\frac{\Delta V}{V_0} = B \times (T_c - 20) + (C + D \times T_c) \times \ln P + E\]  \hspace{1cm} (16)

where \( \frac{B'}{l_0} = B, \ \frac{C'}{l_0} = C, \ \frac{D'}{l_0} = D \)

and \(-\frac{(C' + D' \times 20) \times \ln .001}{l_0} = E\)

Rewriting equation (16) we have

\[V = V_0 \left(1 - (B \times (T_c - 20) + (C + D \times T_c) \times \ln P + E)\right)\]  \hspace{1cm} (17)

which is the equation of state; where \(V_0\) is the specific volume at the standard conditions of 20°C and .001 kbars, \(V\) is the specific volume at pressure \(P\) (kbars) and temperature \(T_c(°C)\) and \(B, C, D\) and \(E\) are the characteristic constants for each plastic, as shown in Table 2.
CHAPTER VII
RESULTS
TABLE 2

Constants For Equation Of State

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Code</th>
<th>Vo (cc/gm)</th>
<th>B (°Cx10^3)</th>
<th>C (x10^-1)</th>
<th>D (°Cx10^-2)</th>
<th>E</th>
</tr>
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<tbody>
<tr>
<td>Nylon 610</td>
<td>1</td>
<td>.869</td>
<td>-.103</td>
<td>.432</td>
<td>.394</td>
<td>.304</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2</td>
<td>1.087</td>
<td>-.281</td>
<td>.450</td>
<td>.853</td>
<td>.323</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3</td>
<td>1.017</td>
<td>-.226</td>
<td>.454</td>
<td>.451</td>
<td>.320</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>4</td>
<td>.848</td>
<td>-.130</td>
<td>.457</td>
<td>.411</td>
<td>.321</td>
</tr>
<tr>
<td>Lexan</td>
<td>5</td>
<td>.850</td>
<td>-.224</td>
<td>.466</td>
<td>.468</td>
<td>.329</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>6</td>
<td>1.081</td>
<td>-.470</td>
<td>.457</td>
<td>1.159</td>
<td>.331</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>7</td>
<td>1.053</td>
<td>-.287</td>
<td>.416</td>
<td>.512</td>
<td>.294</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>8</td>
<td>.893</td>
<td>-.167</td>
<td>.380</td>
<td>.000</td>
<td>.263</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>9</td>
<td>.881</td>
<td>-.159</td>
<td>.353</td>
<td>.501</td>
<td>.251</td>
</tr>
<tr>
<td>FEP</td>
<td>10</td>
<td>.468</td>
<td>-.393</td>
<td>.406</td>
<td>.278</td>
<td>.284</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>11</td>
<td>1.126</td>
<td>-.076</td>
<td>.381</td>
<td>.066</td>
<td>.264</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>12</td>
<td>.708</td>
<td>-.027</td>
<td>.446</td>
<td>.228</td>
<td>.311</td>
</tr>
<tr>
<td>Delrin 100</td>
<td>13</td>
<td>.711</td>
<td>-.208</td>
<td>.346</td>
<td>.585</td>
<td>.247</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>14</td>
<td>1.059</td>
<td>-.361</td>
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<td>.897</td>
<td>.300</td>
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<tr>
<td>Delrin 500X</td>
<td>15</td>
<td>.722</td>
<td>-.125</td>
<td>.296</td>
<td>.000</td>
<td>.204</td>
</tr>
</tbody>
</table>
CHAPTER VIII
DISCUSSION OF RESULTS

In the Data Reduction section a statistical measure of the accuracy of the derived empirical equation of state is given. To further illustrate this, two runs one with a high correlation factor (curve (1)) and one with a lower correlation factor (curve (2)) are plotted in Figures 6 and 7. In figure 6 the displacement data obtained experimentally is plotted against the cell pressure. Both curves (1) and (2), have the same general shape and all points lie on a smooth line. Figure 7 represents a plot of the corrected displacement against InP, using data from the same runs as in Figure 6. From Figure 7 it can be seen that data for curve (1) fits a straight line relationship very well except for the first point. Data for curve (2) also fits a straight line quite well except for the first three points. This effect is expected because frictional forces between the sample, the gaskets and the cylinder walls are significant in this region, and therefore accurate measurements of cell pressure in this region is not possible. However since during computation of the straight line constants 33 experimental points are used, then the effect
FIGURE 6. PLOT OF EXPERIMENTAL DATA

(1) Polyethylene, high density  
(2) Nylon 66
at 25°C
In Figure 7, the straight line fit of experimental data for two materials is shown:

1. Polyethylene, high density
2. Nylon 66

Both are at 25°C.

FIGURE 7. STRAIGHT LINE FIT OF EXPERIMENTAL DATA
of two or three slightly inaccurate points at the low pressure end is negligible. Since the equation of state is found to fit the experimental data so well, the thermodynamic functions are calculated using this equation.

Figure 8 represents a pressure plot of the equation

$$\frac{-\Delta V}{V_0} = B(T_c - 20) + (C + D \times T_c) \ln P + E$$

for a medium density polyethylene, showing the effect of temperature on compression $\frac{-\Delta V}{V_0}$. As the temperature is increased the compression of the plastic is increased. At low pressures, the higher the temperature the lower is $\frac{-\Delta V}{V_0}$ this demonstrates the thermal expansion of the sample.

Bridgman, suggested without any experimental evidence, that the compressibility of plastics could be directly related to their densities, and that further work should be done to ascertain this postulation. In Figures 9 and 10, the compressibility of a number of plastics, with densities ranging from 0.897 to 2.139 gms/cc are plotted against pressure. Figure 9 suggests that compressibility for different plastics is not directly related to density, however compressibility of a certain plastic family such as polyethylene (Figure 10), having different densities, is directly related to its density.
FIGURE 8. EFFECT OF PRESSURE ON COMPRESSION

(1) Polyethylene, low density, at 20°C
(2) Polyethylene, low density, at 50°C
(3) Polyethylene, low density, at 90°C
FIGURE 9. EFFECT OF PRESSURE ON COMPRESSIBILITY

(1) FEP
(2) Polyvinylchloride
(3) Nylon 66
(4) Polypropylene
(5) Polystyrene

at 60°C
(1) Polyethylene, high density  
(2) Polyethylene, med. density  
(3) Polyethylene, low density  

FIGURE 10. EFFECT OF PRESSURE ON COMpressibility
In Figure 11 dilation is plotted against pressure. For a plastic having different densities such as polyethylene, there is a dependence of dilation on density. For chemically different plastics, however, this property is not exhibited.

Typical values of heat and work of compression for different plastics are shown in Figure 12. Such values are used to calculate the change of internal energy as shown in Figures 13 and 14. In all cases a minimum in the internal energy curve is present. Bridgman (14) has proposed that this behaviour in internal energy as the pressure is varied isothermally may be explained on the basis that the intermolecular forces are normally predominantly attractive. On compression the potential energy decreases, and the internal energy, therefore decreases. However, at some compressed volume the process must reverse because the intermolecular forces ultimately become repulsive. Hence on increasing the pressure the internal energy change decreases, then reverse direction, ultimately becoming increasingly positive.

A very interesting and meaningful thermodynamic quantity to consider is the change of entropy with pressure as shown in Figure 15. As the pressure is increased on a
FIGURE 11. EFFECT OF PRESSURE ON DILATION

(6) Polyethylene, low density  (3) Polystyrene
(5) Polyethylene, med. density  (2) "Lexan" at 220°C
(4) Polyethylene, high density  (1) Polypropylene
(1) Polystyrene
(2) Polyethylene, low density at 60°C
(3) FEP

FIGURE 12. EFFECT OF PRESSURE ON HEAT AND WORK

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FIGURE 13. EFFECT OF PRESSURE ON INTERNAL ENERGY

(1) FEP
(2) Polyethylene, low density at 60°C
(3) Polystyrene
(4) Nylon 6
Figure 14. Effect of Pressure on Internal Energy

(1) Polymethylmethacrylate  
(2) Polyvinylchloride  
at 60°C

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FIGURE 15. EFFECT OF PRESSURE ON ENTROPY

\( \Delta S \text{ (cals/gm. } °\text{K) } \)

0 5 10 15 20 25

\( P \) (kbars)

0.000

0.02

0.04

0.06

0.08

0.10

0.12

0.14

(1) FEP
(2) Polystyrene
(3) Polypropylene
(4) Polymethylmethacrylate

at 60 °C

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plastic sample, its volume decreases, resulting in an increase in density. Since crystallinity is directly related to density (4, 5, 6) then upon increasing pressure the crystallinity or the orderliness of the molecules of the sample is increased. This effect is confirmed by the calculated values of the entropy change, since they decrease with increasing pressure indicating a decrease in the randomness of the molecular arrangement of the sample.

From equation (8) it is seen that the change of $C_p$ with respect to pressure is zero, because there are no second order temperature terms in the equation of state. The change of $C_v$ then, can be directly calculated from equation (9), producing results as shown in Figure 16. Since the changes in $C_v$ are very small, and the accuracy of this type of calculations become sensitive to assumptions made in fitting the data to a general equation, then the results represented by Figure 16 should only be considered as qualitative.

The compression of "Teflon" yielded transition points as shown in Figure 17. This was expected since the compression of "Teflon" had been previously studied by a number of investigators. An unusual effect, however, was observed at 120°C and 23 kbars. At this point the volume
FIGURE 16. EFFECT OF PRESSURE ON HEAT CAPACITY

(1) Polyethylene, low density   (3) Nylon 6
(2) Polyethylene, high density   (4) Polypropylene
   at 20°C
All curves except the one at 30°C are displaced upwards from each other by .005 units on the $-\Delta V/\Delta V_0$ axis.

FIGURE 17. COMPRESSION OF "TEFLON"
of the sample decreased at constant pressure indicating a possible phase transition. This effect is not further investigated because the cell was not designed to go above the temperature and pressure conditions of this point. Further work should be done in this region to confirm the existence of a phase transition.

A proposed phase diagram for "Teflon" which agrees quite well with the one obtained by Weir is shown in Figure 18.
FIGURE 18. PROPOSED PHASE DIAGRAM FOR "TEFLON"
CHAPTER IX

CONCLUSIONS

The high pressure cell developed for this experiment withstood pressures of up to 27 kbars, and was continually subjected to pressures of up to 23 kbars. Using a similar method of construction a cell with three or four reinforcing jackets could be developed to withstand pressures perhaps as high as 50 kbars.

The equation of state derived in this thesis is more convenient and reliable than that derived by Weir, since it has no artificial maximum points, arising in successive differentiation of the equation with respect to pressure.

A direct correlation was not found between the density and compressibility for the plastics investigated. However an ordered relationship exists between the compressibility and density of a particular plastic series such as different density polyethylenes.

None of the plastics tested with the exception of "Teflon" exhibited phase transitions. "Teflon" yielded results comparable to those obtained by previous workers.
There also was an indication of a pressure induced phase change in "Teflon" at 120°C and approximately 23 kbars.
BIBLIOGRAPHY

APPENDIX A

Pressure Units

1 bar = $10^6$ dynes/cm$^2$

= 0.987 atm.

= 1.019 kgm/cm$^2$

= 14.406 psi
APPENDIX B

Specifications For "Carboloy"

<table>
<thead>
<tr>
<th>Grade</th>
<th>Use</th>
<th>55A</th>
<th>883</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cell cylinder</td>
<td>Cell pistons</td>
<td></td>
</tr>
<tr>
<td>Chemical composition (% by wt.)</td>
<td>WC 87.0, Co 13.0</td>
<td>WC 94.0, Co 6.0</td>
<td></td>
</tr>
<tr>
<td>Hardness (Rockwell A)</td>
<td>88.3</td>
<td>92.0</td>
<td></td>
</tr>
<tr>
<td>Density (gm/cc)</td>
<td>14.20</td>
<td>14.95</td>
<td></td>
</tr>
<tr>
<td>Transverse rupture strength (psi)</td>
<td>328,000</td>
<td>220,000</td>
<td></td>
</tr>
<tr>
<td>Ultimate strength in compression (psi)</td>
<td>530,000</td>
<td>614,000</td>
<td></td>
</tr>
<tr>
<td>Ultimate strength in tension (psi)</td>
<td>210,000</td>
<td>205,000</td>
<td></td>
</tr>
<tr>
<td>Elastic limit in compression (psi)</td>
<td>78,000</td>
<td>286,000</td>
<td></td>
</tr>
<tr>
<td>Elastic limit in tension (psi)</td>
<td>88,000</td>
<td>200,000</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX C

CONSTRUCTION OF HIGH PRESSURE CELL

jacket no. 2, hardened steel, (SPS245), shrink fitted on jacket no. 1 and "Carboloy" cylinder

jacket no. 1, hardened steel, (SPS245), shrink fitted on "Carboloy" cylinder

"Carboloy" cylinder

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APPENDIX D

Experimental Data

The original experimental data is available on computer cards from the Department of Chemical Engineering, University of Windsor, Windsor, Ontario.
VITA AUCTORIS

1943  Born in Cairo, Egypt.

1955  Completed elementary education at Armenian National School, Cairo, Egypt.

1959  Completed Grade XIII in Patterson Collegiate Institute, Windsor, Ontario.

1963  Received the Degree of Bachelor of Applied Science in Chemical Engineering from Assumption University of Windsor, Windsor, Ontario.

1965  Currently, a candidate for the Degree of Master of Applied Science at the University of Windsor, Windsor, Ontario.