Experimental diffusivity and solubility of carbon dioxide and nitrogen in polypropylene

Pawan Kundra
Ryerson University

Follow this and additional works at: http://digitalcommons.ryerson.ca/dissertations
Part of the Chemical Engineering Commons

Recommended Citation
EXPERIMENTAL DIFFUSIVITY AND SOLUBILITY OF CARBON DIOXIDE AND NITROGEN IN POLYPROPYLENE

By

Pawan Kundra

Bachelor of Engineering

Punjab Technical University (PTU)

Punjab, India, 2003

A thesis

presented to Ryerson University

in partial fulfillment of the requirement for the degree of Master of Applied Science

in Chemical Engineering

Toronto, Ontario, Canada, 2008

© Pawan Kundra, 2008
Author’s Declaration

I hereby declare that I am the sole author of this thesis.

I authorize Ryerson University to lend this thesis to other institutions or individuals for the purpose of scholarly research.

I further authorize Ryerson University to produce this thesis by photocopying or by other means, in total or part, at the request of other institutions or individuals for the purpose of scholarly research.
Abstract

Experimental Diffusivity and Solubility of Carbon Dioxide and Nitrogen in Polypropylene

Pawan Kundra

Master of Applied Science, 2008
Directed by: Dr. Simant R. Upreti, Dr. Ali Lohi, Dr. Jiangning Wu
Department of Chemical Engineering,
Ryerson University, Toronto

In this work, we determined the concentration-dependent diffusivity and solubility of environmentally benign blowing agents, carbon dioxide and nitrogen in polypropylene. For this purpose, experiments were carried out to obtain pressure decay data in the range 170–190°C and 0.29–7.32 MPa. For each experimental run, the mass of gas absorbed as a function of time led to the calculation of diffusion coefficient. The equilibrium pressure at sufficiently long time enabled the calculation of solubility. The calculus of variation was used to establish the necessary conditions for the determination of concentration-dependent diffusivity such that the model-predicted mass of gas absorbed in polymer matches with the experimental counterpart. The value of diffusivity was found to lie in the ranges 2.67–9.13×10⁻⁹ and 3.88–12.94×10⁻⁹ m² s⁻¹ for carbon dioxide and nitrogen, respectively.
Acknowledgment

I am deeply indebted to my supervisors, Drs. Simant R. Upreti, Ali Lohi, and Jiangning Wu for their valued supervision, support and guidance during my M.A.Sc. period. I would like to convey my sincere thanks to everyone who helped, support and encourage me throughout this study in every way possible.

My special thanks go to Dr. Simant R. Upreti for giving me an opportunity to work on this project and also for his excellent guidance along with inspiration throughout the thesis work.

I appreciate the indisputable support that I received from the mechanical workshop team Mr. Ali Hemmati, and Mr. Peter Scharping during the equipment setup. I also appreciate the support I received from the electrical lab supervisor—Mr. Tondar Tajrobehkar. Without their support it would not be possible for me to complete this experimental research.

I also would like to thank Canada Foundation of Innovation, Ontario Innovation Trust, Natural Sciences and Engineering Research Council of Canada, and Department of Chemical Engineering, Ryerson University for funding this project.
# Table of Contents

Author's Declaration ...................................................................................................................... ii  
Abstract ........................................................................................................................................ iii  
Acknowledgment ........................................................................................................................... iv  
Table of Contents ............................................................................................................................. v  
List of Tables ................................................................................................................................... viii  
List of Figures ................................................................................................................................. ix  
Nomenclature .................................................................................................................................. xii  
Instruction for Borrowers .............................................................................................................. xiv

1 Introduction ............................................................................................................................ 1  
   1.1 Diffusion and Devolatilization .......................................................................................... 2  
   1.2 Diffusion and Plasticization ......................................................................................... 3  
   1.3 Diffusion and Foaming .................................................................................................. 4  
   1.4 Candidate Polymer ...................................................................................................... 7  
   1.5 Purpose and scope of this study .................................................................................. 9  
   1.6 Outline of Thesis .......................................................................................................... 10

2 Literature Review ..................................................................................................................... 11  
   2.1 Diffusivity ..................................................................................................................... 11  
   2.2 Experimental approaches for measurement of diffusion coefficient ......................... 12  
       2.2.1 Direct Methods ........................................................................................................ 13  
           2.2.1.1 Quartz Spring Apparatus ............................................................................. 13  
           2.2.1.2 Magnetic Suspension Balance ....................................................................... 15  
       2.2.2 Indirect Methods .................................................................................................... 18  
           2.2.2.1 Piezoelectric Sorption Method .................................................................... 18
List of Tables

2-1: Diffusivity data generated by using Quartz Spring Apparatus ............................... 14
2-2: Diffusivity data generated by using Magnetic Suspension Balance ................... 17
2-3: Diffusivity data generated by using Pressure decay method ............................. 19
3-1: Experimental Summary ....................................................................................... 34
5-1: Peak diffusivity values of carbon dioxide in polypropylene at experimental temperatures and pressures ................................................................. 59
5-2: Peak diffusivity values of nitrogen in polypropylene at experimental temperatures and pressures ................................................................. 64
5-3: Parameters for mathematical correlation Equation (5.1) at different temperatures for carbon dioxide gas ........................................................................ 77
5-4: Parameters for mathematical correlation Equation (5.1) at different temperatures for nitrogen gas ......................................................................................... 78
C-1: Specific volume of Carbon dioxide at different temperatures and pressures .......... 100
C-2: Specific volume of Nitrogen at different temperatures and pressures ................. 101
D-1: Solubility data of Carbon dioxide and Nitrogen in polypropylene at experimental temperatures and pressures ................................................................. 102
List of Figures

1-1: Ozone depleting potential (ODP) of CFCs, HCFCs, CO₂ and N₂...........................................6
1-2: Global warming potential (GWP) of CFCs, HCFCs, CO₂ and N₂...........................................6
1-3: World polymer demand (in percentage) by 2007.................................................................8
2-1: Schematic diagram of Magnetic Suspension Balance..........................................................16
2-2: Concentration dependent diffusivity of toluene in polystyrene........................................21
2-3: Diffusion coefficient versus temperature diagram of methane-polystyrene and ethyl benzene-polystyrene systems.................................................................23
3-1: Schematic diagram of pressure vessel.................................................................................27
3-2: Picture of pressure vessel......................................................................................................27
3-3: Schematic diagram of the experimental set-up......................................................................29
3-4: Photograph of syringe pump used to compress gas at desired pressure............................30
3-5: Photograph of Experimental set-up for pressure decay system........................................31
3-6: Pressure decay plot of carbon dioxide in polypropylene at initial pressure of 0.454 MPa 170°C..................................................................................................................................................35
3-7: Experimental pressure drop of carbon dioxide gas at different pressures at 180°C ........37
3-8: Sample after experimental runs at 180°C with Carbon dioxide........................................37
4-1: Unidirectional Mass transfers of gas in polymer melt.........................................................39
4-2: Cubic spline interpolations for PVT data of gases at experimental pressure....................44
4-3: Cubic spline interpolations for PVT data of gases at experimental temperature...............44
4-4: Solution methodology for diffusivity calculation.................................................................53
4-5: Extent of minimization of objective function.........................................................................54
5-1: Concentration dependent diffusivity of carbon dioxide in polypropylene at various pressures at 170°C ..................................................................................................................56
5-2: Concentration dependent diffusivity of carbon dioxide in polypropylene at different pressures at 180°C ..................................................................................................................57
5-3: Concentration dependent diffusivity of carbon dioxide in polypropylene at different pressures at 190°C ..................................................................................................................58
5-4: Concentration dependent diffusivity of nitrogen in polypropylene at different pressures at 170°C .................................................................................................................................61
5-5: Concentration dependent diffusivity of nitrogen in polypropylene at different pressures at 180°C ................................................................. 62
5-6: Concentration dependent diffusivity of nitrogen in polypropylene at different pressures at 190°C ................................................................. 63
5-7: Temperature effect on diffusivity of nitrogen in polypropylene ................................................................. 66
5-8: Temperature effect on diffusivity of carbon dioxide in polypropylene ................................................................. 67
5-9: Solubility of carbon dioxide in polypropylene at different temperatures ................................................................. 70
5-10: Solubility of nitrogen in polypropylene at different temperatures ................................................................. 71
5-11: Comparison of solubility of carbon dioxide with nitrogen in polypropylene at experimental temperatures and pressures ................................................................. 72
5-12: Sensitivity analysis to gas volume change of carbon dioxide gas at 0.29 MPa 180°C ....... 73
5-13: Sensitivity analysis to gas volume change of nitrogen gas at 1.85 MPa 180°C ................................................................. 74
A-1: Pressure decay plot of carbon dioxide at 1.440 MPa 170°C ................................................................. 85
A-2: Pressure decay plot of carbon dioxide at 2.350 MPa 170°C ................................................................. 86
A-3: Pressure decay plot of carbon dioxide at 3.710 MPa 170°C ................................................................. 86
A-4: Pressure decay plot of carbon dioxide at 6.770 MPa 170°C ................................................................. 87
A-5: Pressure decay plot of carbon dioxide at 0.291 MPa 180°C ................................................................. 87
A-6: Pressure decay plot of carbon dioxide at 0.990 MPa 180°C ................................................................. 88
A-7: Pressure decay plot of carbon dioxide at 1.856 MPa 180°C ................................................................. 88
A-8: Pressure decay plot of carbon dioxide at 2.785 MPa 180°C ................................................................. 89
A-9: Pressure decay plot of carbon dioxide at 4.100 MPa 180°C ................................................................. 89
A-10: Pressure decay plot of carbon dioxide at 5.430 MPa 180°C ................................................................. 90
A-11: Pressure decay plot of carbon dioxide at 6.780 MPa 180°C ................................................................. 90
A-12: Pressure decay plot of carbon dioxide at 1.425 MPa 190°C ................................................................. 91
A-13: Pressure decay plot of carbon dioxide at 2.670 MPa 190°C ................................................................. 91
A-14: Pressure decay plot of carbon dioxide at 5.450 MPa 190°C ................................................................. 92
A-15: Pressure decay plot of nitrogen at 0.994 MPa 170°C ................................................................. 92
A-16: Pressure decay plot of nitrogen at 2.977 MPa 170°C ................................................................. 93
A-17: Pressure decay plot of nitrogen at 0.733 MPa 180°C ................................................................. 93
A-18: Pressure decay plot of nitrogen at 1.256 MPa 180°C ................................................................. 94
A-19: Pressure decay plot of nitrogen at 1.987 MPa 180°C ................................................................. 94
A-20: Pressure decay plot of nitrogen at 2.124 MPa 180°C ................................................................. 95
A-21: Pressure decay plot of nitrogen at 3.090 MPa 180°C ................................................................. 95
A-22: Pressure decay plot of nitrogen at 6.753 MPa 180°C ................................................................. 96
A-23: Pressure decay plot of nitrogen at 2.009 MPa 190°C ................................................................. 96
A-24: Pressure decay plot of nitrogen at 4.310 MPa 190°C ................................................................. 97
A-25: Pressure decay plot of nitrogen at 5.350 MPa 190°C ................................................................. 97
Nomenclature

\( a_i \) Parameters of equation (5.1); \((i = 0,1,\ldots,9)\)

\( A \) Cross-section area of the polymer layer, \( \text{m}^2 \)

\( d \) Internal diameter of the pressure vessel, m

\( D \) Diffusivity of gas in polymer, \( \text{m}^2 \text{s}^{-1} \)

\( F \) Augmented objective functional

\( I_{\text{min}} \) Objective functional

\( J \) Rate of transfer per unit area kg, \( \text{m}^{-2} \text{s}^{-1} \)

\( K \) Augmented objective functional

\( L \) Thickness of the polymer sample, m

\( m_{\text{gp,m}} \) Calculated mass of gas absorbed in the polymer layer, Kg

\( m_{\text{gp,e}} \) Experimental mass of gas absorbed in the polymer layer, Kg

\( M_n \) Number average molecular weight of polymer, kg K mol\(^{-1}\)

\( M_w \) Weight average molecular weight of polymer, kg K mol\(^{-1}\)

\( N \) Molar flux of gas, kg mol m\(^{-2}\) s\(^{-1}\)

\( P \) Pressure, MPa
$P_{exp}$  Experimental Pressure, MPa

$P_f$  Final Pressure, MPa

$P_i$  Initial Pressure, MPa

$\Delta P$  Pressure Drop, MPa

$T$  Total experimental run time, s

$T_{exp}$  Experimental temperature, °C

$z$  Depth in the polymer layer, m

$\rho$  Density of polymer sample, kg m$^{-3}$

$\lambda$  Adjoint variable

$\omega$  Gas mass concentration in the polymer, kg m$^{-3}$

$\omega_{sat}$  Saturated $\omega$, kg m$^{-3}$
Instruction for Borrowers

Ryerson University requires the signatures of all persons using or photocopying this thesis.

Please sign below, and give address and date.

<table>
<thead>
<tr>
<th>Name</th>
<th>Signature</th>
<th>Address</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1 Introduction

The polymer industry has seen a phenomenal growth in the last century, and this growth has been continuing at a rate faster than any other chemical industry. The process of converting monomers to polymers by processes such as residual monomer stripping, bulk phase separation, devolatilization and further processing of polymers to finished commercially useful articles by processes such as plasticization and foaming involves transport phenomena, which is quite complex. A transport property known as diffusion has attracted interests of chemical engineers working in polymer industry.

The measurement of the diffusion of relatively low molecular weight penetrants in polymers provides a convenient method of determining the nature of the kinetic agitation of polymer molecules. In addition, such diffusion measurements are needed for the design of polymer processing equipment for molten polymers. For example, the diffusion of monomers, catalysts, diluents, or by-products can have a significant influence on the behavior of polymerization reactors. In addition, a processing step involving the removal of residual components from polymers often succeeds these reactors. The distribution of blowing agents, plasticizers, and other additives in molten polymers is often strongly dependent on molecular diffusion. Finally, the utilization of polymers in packing or as protective coatings is usually based on how well the polymers resist the diffusion of penetrants. Hence the need to address the issue of diffusion in polymer system is very important.
1.1 Diffusion and Devolatilization

In the polymerization processes of converting monomers to polymers it is common for them to contain impurities which are unwanted in final products made from the polymers. Such impurities typically include residual monomers and low molecular weight organic species such as dimmers and trimmers that may be formed during the polymerization process. These substances collectively referred to as volatiles and they are undesired in polymers. Their concentration can be as low as ppm or as high as several tens of percent. Separation of volatiles from polymer may be preferred for several reasons, such as

- To recover unconverted monomers
- To fulfill health and environmental regulations
- To increase the rate of conversion
- To eliminate potential odors

The process by which volatiles are separated from the bulk polymer is called devolatilization. Devolatilization is a complex process involving:

- The transport of volatiles to a polymer-vapor interface
- Evaporation of the volatiles at the interface
- Their subsequent removal by a vacuum system

The slowest process is the rate-controlling process. Usually it the transports of volatile to polymer-vapor interface, which can progress through a foaming mechanism. In the devolatilization process, a molten polymer is mixed with a small amount of an inert substance known as stripping agent such as water, carbon dioxide, or nitrogen. This causes a large
population of bubbles in the molten polymer mass. Due to this there will be shorter diffusion
distances for volatiles and large interfacial transport areas afforded by swarms of bubbles within
the polymer melt. This yields much higher devolatilization rates. The importance of the role of
diffusion and knowledge of molecular diffusivities in understanding devolatilization
mechanisms is evident. Consequently, the designs of these devolatilization processes require
information concerning the diffusion coefficients of these stripping agents.

1.2 Diffusion and Plasticization

A plasticizer is a substance incorporated in a material to increase its flexibility or workability.
Generally, there are two types of plasticizers, internal and external. When we use a plasticizer
for chemical modification for the structure of the polymer, we refer to it as internal
plasticization. On the other hand when we add a plasticizer to a polymer matrix, which positions
itself between the intermolecular bonds of the polymer and increases the spacing between
adjacent bonds, which bring the changes on flexibility or workability of the polymer are known
as external plasticizers. Our focus for this research is limited to external plasticizers only.

Plasticizers have several unique advantages in polymer processing. Plasticizers allow a
polymeric material to flow more uniformly under less mechanical shear and at lower
temperatures. Kwag [1998] has shown that incorporation of a small amount of carbon dioxide
(3–5%) in a polymer melt decreases the viscosity of the polymer by about 2–3 orders of
magnitude. This not only reduces energy cost, but also improves the efficiency of process.
Softening effect of plasticizers is the same as that of an increase in temperature, thus there is a
smaller danger of thermal degradation. In this respect plasticizers are indirectly thermal
stabilizers [Robert, 2000].
Different types of organic plasticizers have been used in polymer processing. As they have harmful effects on the environment, the use of carbon dioxide and nitrogen which are non-corrosive, inexpensive and environmentally benign as external plasticizers eliminates the disadvantages associated with organic plasticizers. Carbon dioxide is a gas under atmospheric conditions; it can be used as a plasticizer and then easily removed from the polymer through evaporation to obtain the original physical properties of the polymer matrix [Robert, 2000]. While carbon dioxide is known to be an effective plasticizer for polymers, very little is known about the diffusion mechanism and the resulting change in rheology.

1.3 Diffusion and Foaming

Generally, there are two types of foaming agents: Chemical Blowing Agents (CBAs) and Physical Blowing Agents (PBAs). CBAs are individual compounds or mixtures that release gases (such as N\textsubscript{2}, and \textit{CO}\textsubscript{2}) as a result of chemical reactions and most of CBAs are solids. PBAs are compounds that release gases as a result of physical processes (e.g. evaporation, desorption) at elevated temperature or reduced pressure. Most PBAs are volatile chemicals such as chlorofluorocarbons (CFCs) and hydrocarbons (HCs). Among them, CFCs were most widely used in the foam industry. However, due to ozone depleting and the global warming potentials [refer to Figures 1.1 and 1.2] the use of CFCs and their derivatives such as hydrochlorofluorocarbons (HCFCs) is restricted.

The Ozone Depleting Potential (ODP) is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11. Thus, the ODP of CFC-11 is defined as 1.0. The Global Warming Potential (GWP) represents how much a given mass of a chemical
contributes to global warming over a given time period compared to the same mass of carbon
dioxide. Carbon dioxide’s GWP is defined as 1.0.

Currently, three types of material have the potential to replace CFCs and HCFCs. The first are
hydrofluorocarbons (HFCs). They have no known effects on the ozone layer. However, HFCs
are expensive and categorized as greenhouse gases and some HFCs are flammable. The second
are hydrocarbons (HCs). They are considered fire hazards due to their high flammability and
volatile nature. The third type is inert gases, e.g. carbon dioxide and nitrogen. Carbon dioxide
has zero ozone depleting potential and one global warming potential. Nitrogen has zero ozone
depleting and global warming potential.

The polymer industry is slowly implementing carbon dioxide and nitrogen as a low-cost, safe
and environmentally friendly PBAs alternates to CFCs and HCFCs. Carbon dioxide often
changes from a liquid to either a gas or supercritical fluid within a foaming process. Any of the
three phases can be used for foaming. Carbon dioxide and nitrogen have lower solubility than
most PBAs (such as CFCs and HCFCs), but it is high enough to produce the foams [Kwag,
1998]. However, the progress of implementing carbon dioxide and nitrogen as PBAs is slow due
to several obstacles, ranging from lack of diffusivity data to quantitative understanding of the
influence of carbon dioxide and nitrogen on viscosity of the polymer.
**Figure 1-1:** Ozone depleting potential (ODP) of CFCs, HCFCs, CO₂ and N₂

[United States Environmental Protection Agency, 2007]

![Figure 1-1: Ozone depleting potential (ODP) of CFCs, HCFCs, CO₂ and N₂](image1)

**Figure 1-2:** Global warming potential (GWP) of CFCs, HCFCs, CO₂ and N₂

[United States Environmental Protection Agency, 2007]

![Figure 1-2: Global warming potential (GWP) of CFCs, HCFCs, CO₂ and N₂](image2)
1.4 Candidate Polymer

Polypropylene was discovered in the early 1950s. Since then polypropylene has grown to a commodity polymer with numerous grades for specific end uses. By controlling the polymer chemistry it is now feasible to generate a range of polypropylenes possessing different mechanical properties. Another major advantage of using polypropylene is the recyclability of the polymer which is becoming an important issue. In normal circumstances polypropylene obtained after recycling is usually blended with virgin polypropylene and is again used for similar applications [Harper, 1999]. As per information from Chemical Market Associates Inc., world polymer demand for 2007 was 183 million metric tons and almost one fourth of this demand was polypropylene [refer to Figure 1.3].

As polypropylene is colorless, non-toxic, and translucent to transparent solid with a glossy surface, it is mainly used for packaging including food packaging, where we use HCFCs during devolatilization and foaming of polypropylene which are harmful and can be replaced with environmentally benign alternatives such as carbon dioxide, and nitrogen.
Figure 1-3: World polymer demand (in percentage) by 2007

[Chemical Market Associates Inc.]
1.5 Purpose and scope of this study

The objective of the research was to determine concentration dependent diffusivity of carbon dioxide and nitrogen in polypropylene at different temperatures and pressures. Although the molecular diffusion of solvents in molten polymers is important in many polymer processes, relatively few studies have been concerned with the measurement of diffusion coefficients and solubility under the conditions of interest in the processing of polymer melts. The experimental problems associated with conducting diffusion studies in molten polymers at elevated temperatures and pressures are no doubt partially responsible for the existing deficiency in diffusivity data.

The purpose of this study is to measure the diffusion coefficients and solubility of environmentally benign solvents such as carbon dioxide and nitrogen in polypropylene melt by using pressure decay method. This non-intrusive experimental method is based on the fact that the system pressure decays as the molecular diffusion of solvent into polymer melt proceeds in a closed pressure vessel. Such a process continues until the polymer melt is completely saturated with the solvent. In this experimental technique, the pressure decay of the solvent is accurately measured at constant temperature. With the measured pressure versus time data and a theoretical model for concentration dependent diffusion coefficient, the respective molecular diffusion coefficients of carbon dioxide and nitrogen in polypropylene melt are determined at the constant temperature.
1.6 Outline of Thesis

This thesis is composed of six chapters. Chapter 1 gives an introduction to the thesis research topic together with the purpose and scope of this study for the determination of diffusion coefficient of a gas in polymer. Chapter 2 reviews the concept of diffusivity and various experimental methods available for the determination of diffusion coefficient and solubility of a gas in a polymer. This chapter also includes the research objective of this study. Chapter 3 presents the experimental set up and procedure for conducting the pressure decay measurement of a solvent in a polymer. This chapter also provides experimental summary and observations during experimental runs. Chapter 4 presents the mathematical model and solution methodology for determining the diffusion coefficient. Chapter 5 discusses the diffusivity and solubility results for carbon dioxide and nitrogen in polypropylene. This chapter also presents the effect of temperature and pressure on diffusivity and solubility. A mathematical correlation for diffusivity calculation has been provided in this chapter. Finally, Chapter 6 contains a summary of major conclusions of this thesis study and some recommendations for further study.
2 Literature Review

This chapter reviews the concept of diffusivity, experimental approaches for its determination in polymers along with the data generated are discussed in this chapter. At the end, the concentration and temperature dependence of diffusivity is examined.

2.1 Diffusivity

In 1855, Adolf Euler Fick a German physiologist, proposed the law of diffusion which is stated as “The mathematical theory of diffusion in substances is based on the hypothesis that the rate of transfer of diffusing substances through unit area of a section is proportional to the concentration gradient measured normal to the section” [Crank and Park, 1968]. Fick’s first law of diffusion is mathematically expressed as:

\[ J = -D \frac{\partial \omega}{\partial z} \]  

(2.1)

In Equation (2.1), \( J \) is the rate of transfer per unit area of section, \( \omega \) is the concentration of diffusing substance, and \( z \) is the space co-ordinate measured normal to the cross-section. \( D \) is the diffusivity of substance in the medium.

Once the mass-balance of an element is taken into consideration, Equation (2.1) can be used to derive the fundamental differential equation of diffusion, where \( D \) is constant [Crank and Park, 1968]:

11
\[ \frac{\partial \omega}{\partial t} = D \left( \frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} + \frac{\partial^2 \omega}{\partial z^2} \right) \]  

(2.2)

In polymeric systems, the diffusion coefficient largely depends on the concentration [Duda, 1985]. The diffusion coefficient in polymeric system varies from point to point and equation (2.2) is more accurately expressed as [Crank and Park, 1968]:

\[ \frac{\partial \omega}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \omega}{\partial x} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial \omega}{\partial y} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial \omega}{\partial z} \right) \]  

(2.3)

Many times a gradient of concentration is present and diffusion occurs only along one direction. In that case, Equation (2.3) reduces to [Crank and Park, 1968]:

\[ \frac{\partial \omega}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \omega}{\partial x} \right) \]  

(2.4)

Equation (2.4) is commonly referred to as Fick’s second law of diffusion. In Equation (2.4) \( D \) is a function of \( x \) and \( \omega \) [Crank and Park, 1968]. With this background, the existing experimental methods for diffusivity determination in polymers would be examined.

### 2.2 Experimental approaches for measurement of diffusion coefficient

Since 1940s, numerous efforts have been made to investigate diffusion coefficient and solubility of a gas in polymer melt simultaneously from a single sorption experiment. There are various direct and indirect experimental methods for diffusion coefficient and solubility calculations. The methods in which measurement of the weight gain of the polymer exposed to the gas are known as direct methods. While the methods in which measurement of one of the parameter of
the system can be converted into mass of absorbed gas are known as indirect methods. The measurement of weight gain with respect to time gives the rate of mass transfer of gas in polymer which is the diffusion coefficient, and the total weight of gas transferable to the polymer is solubility. Each method has its applications and suitability.

2.2.1 Direct Methods

The simplest method is based on direct weighing of the polymer. In this method diffusivity and solubility of a gas in a polymer sample is measured by placing the polymer sample in a pressure vessel, degas the system, and then pressurize it with the desired gas. The sample is weighed until a constant weight is obtained. From these weighted data points, the diffusion coefficient and equilibrium solubilities are obtained. Crank and Park [1949], and Park G.S [1951] utilized this simplest method for diffusion in Polystyrene.

2.2.1.1 Quartz Spring Apparatus

In 1968 Crank and Park described a quartz spring apparatus by which the errors in the simple direct weighing method can be overcome by measuring the polymer mass directly by suspension from a quartz spring and error due to air barrier can be overcome by using vacuum methods. This method was later modified in 1973 by Duda et al. in which he included systems for temperature control and penetrant pressure control. This apparatus makes it possible to obtain very accurate sorption data so that the concentration dependence of the diffusion coefficient can be determined by using the complete sorption curve. For each sorption run, data of the weight pickup as a function of time lead directly to the calculation of diffusion coefficients, where as the equilibrium weight at the very long times can be used to calculate the solubility of the
solvent into the polymer at the temperature and pressure under consideration. Table 2.1 lists the diffusivity data generated by using Quartz Spring Apparatus.

**Table 2-1: Diffusivity data generated by using Quartz Spring Apparatus**

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>Polymer Solvent system</th>
<th>Temp. Range (°C)</th>
<th>Diffusivity x10¹¹ (m² s⁻¹)</th>
<th>Weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polystyrene–n-Pentane</td>
<td>140–170</td>
<td>0.259–1.70</td>
<td>0.007–0.010</td>
</tr>
<tr>
<td></td>
<td>[Duda and Vrentas, 1968]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Polystyrene–Ethyl benzene</td>
<td>160–178</td>
<td>1.2–40</td>
<td>0.0–0.15</td>
</tr>
<tr>
<td></td>
<td>[Duda et al. 1973]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Polystyrene–Ethyl benzene</td>
<td>115–178</td>
<td>0.09–50</td>
<td>0.0–0.7</td>
</tr>
<tr>
<td></td>
<td>[Duda and NI, 1978]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Polystyrene–Toluene</td>
<td>110–178</td>
<td>0.1–20</td>
<td>0.0–0.8</td>
</tr>
<tr>
<td></td>
<td>[Duda et al. 1979]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Polyethylene–O-xylene</td>
<td>125–175</td>
<td>0.0006–50</td>
<td>0.0–0.4</td>
</tr>
<tr>
<td></td>
<td>[Duda et al. 1982]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.1.2 Magnetic Suspension Balance

The magnetic suspension balance is a contactless measurement instrument. The operating mechanism of magnetic suspension balance consists of an electronically controlled magnetic suspension coupling, which is used to transmit the measured force from the sample enclosed in a pressure balance to a microbalance [refer to Figure 2.1]. The suspension magnet which is used for the transmitting the force, consists of a permanent magnet, a sensor core and a device for decoupling the measuring load. An electromagnet, which is attached at the under floor weighing hook of a balance, maintains the freely suspended state of the suspension magnet via an electronic control unit. Using this magnetic suspension coupling, the measuring force is transmitted contactlessly from the measuring chamber to the microbalance, which is located outside the chamber under ambient atmospheric conditions. Table 2.2 lists the diffusivity data generated by using Magnetic suspension balance.
Figure 2-1: Schematic diagram of Magnetic Suspension Balance [Sato et al. 2001]
Table 2-2: Diffusivity data generated by using Magnetic Suspension Balance

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>Polymer Solvent system</th>
<th>Temp. Range (°C)</th>
<th>Diffusivity $\times 10^{11}$ (m$^2$ s$^{-1}$)</th>
<th>Weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly (vinyl acetate), Polystyrene–Carbon dioxide</td>
<td>40–200</td>
<td>0.002–0.990</td>
<td>0.005–0.258</td>
</tr>
<tr>
<td></td>
<td>[Sato et al. 2001]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Poly (butylene succinate), Poly (butylene succinate-co-adipate)–Carbon dioxide</td>
<td>50–180</td>
<td>68.1–268.0</td>
<td>0.009–0.150</td>
</tr>
<tr>
<td></td>
<td>[Sato et al. 2000]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>LDPE, HDPE, PP, PS–Supercritical Carbon dioxide</td>
<td>150–200</td>
<td>1–11</td>
<td>0.001–0.090</td>
</tr>
<tr>
<td></td>
<td>[Areerat et al. 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Poly(vinyl acetate)–methanol–toluene</td>
<td>20–60</td>
<td>0.0004–0.053</td>
<td>0.004–0.330</td>
</tr>
<tr>
<td></td>
<td>[Mamaliga et al. 2004]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.2 Indirect Methods

When the amount of diffusant absorbed by a polymer specimen is very small, measurements of the increase in mass yield dubious values of the equilibrium sorption and indicates little about the sorption kinetics. Under these conditions, measurement of one of the parameters, like frequency of a crystal in piezoelectric sorption method, or pressure measurement in pressure decay method and then converting that into mass of absorbed gas can provide valuable information.

2.2.2.1 Piezoelectric Sorption Method

In 1975, Chang and Bonner devised a piezoelectric sorption method to determine gas solubility in polymers at high pressure. In this method, firstly the frequency of clean uncoated crystal is determined. Then after, the crystal is coated with the polymer and exposed to the gas under consideration at desired temperature and pressure. It is based on the principle that the frequency of the crystal increases with increase in mass of the polymer coated on the crystal. Therefore the relevant frequency of the crystal can be applied to determine diffusivity and solubility of gas dissolved in polymer coating layer on the surface of crystal. Chang and Bonner [1977] used this method for solubility determination of Ethylene in Low-density polyethylene. The major problem with this method is due to polymer sample's viscosity change it can't be applied at a high temperature.

2.2.2.2 Pressure decay Method

Pressure decay method is relatively popular because the apparatus is simple, easy to operate and the installation costs are reasonable. The pressure decay method is the most popular technique for sorption measurement at high temperature and pressures. This technique was first developed
by Newitt and Weale in 1948 for experimental measurement of gases solubility in polystyrene melt.

The principle of the experiment is to constrain liquid polymer in a steel cylinder and place it in a pressure vessel in a closed system of known volume. The pressure vessel is brought to the temperature of the experiment. Preheated gas is admitted, the system is closed quickly, and pressure is measured as a function of time until a constant pressure, indicating the completion of sorption is reached. The requirements for an accurate estimate of solubility and diffusivity from a sorption experiment are accurate pressure measurements at very short elapsed times, leak proof pressure vessel and careful thermostatting of the system. Table 2.3 lists the diffusivity data generated by using pressure decay method.

**Table 2-3:** Diffusivity data generated by using Pressure decay method

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>Polymer Solvent system</th>
<th>Temp. Range (°C)</th>
<th>Diffusivity x10⁹ (m² s⁻¹)</th>
<th>Weight fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyethylene–Nitrogen  [Lundberg et al. 1960]</td>
<td>125–225</td>
<td>2.8–4.5</td>
<td>0.003–0.025</td>
</tr>
<tr>
<td>2</td>
<td>Polyethylene–Methane   [Lundberg et al. 1962]</td>
<td>125.8–226.1</td>
<td>2.85–3.2</td>
<td>0.004–0.025</td>
</tr>
<tr>
<td>3</td>
<td>Polystyrene–Methane    [Lundberg et al. 1963]</td>
<td>100–188</td>
<td>0.046–0.48</td>
<td>0.008–0.031</td>
</tr>
<tr>
<td>4</td>
<td>Linear Polyethylene–Methane [Lundberg, 1964]</td>
<td>140–188.3</td>
<td>1.5–3.6</td>
<td>0.005–0.060</td>
</tr>
<tr>
<td>5</td>
<td>Polyethylene–Nitrogen Polyisobutylene–Helium Polypropylene–CO₂ [Durill and Griskey, 1966]</td>
<td>188</td>
<td>4.02–17.09</td>
<td>0.003–0.052</td>
</tr>
<tr>
<td>6</td>
<td>LDPE–Nitrogen, Ethylene, CO₂ [Davis et al. 2004]</td>
<td>150</td>
<td>2.7–8.0</td>
<td>0.002–0.032</td>
</tr>
</tbody>
</table>
2.3 Concentration dependence of diffusion coefficient

At low solvent concentration, there is a strong dependence of diffusivity on the concentration of solvent [Duda et al. 1982]. Figure 2.2 shows the general concentration dependent diffusivity behavior. The actual range of the concentration depends on the characteristics of the polymer-solvent system. As indicated, the diffusion coefficient sharply increases with solvent concentration and often exhibits a maximum value in the concentrated region. At low solvent concentrations, a small increase in the solvent weight fraction will cause a very significant increase in the available free volume and a correspondingly large increase in the diffusion coefficient [Duda, 1985]. The maximum diffusion coefficient of solvent in a polymer increases with increase in temperature. It can be concluded that rather than being an averaged single point value, diffusivity has a behavior dependency on concentration.

In most cases, the variation of diffusivity with solvent concentration is decreased as the size of the molecule decreases. Investigations of diffusion phenomena in polymer-solvent systems [Biesenberger, 1983] have shown that it is possible to observe widely differing behavior by traversing a large enough range of concentration, temperature and polymer molecular weight.
Figure 2-2: Concentration dependent diffusivity of toluene in polystyrene [Duda et al. 1982]
2.4 Temperature dependence of diffusion coefficient

Diffusion coefficients of liquid systems composed of relatively low molecular weight molecules usually fall in the magnitude range of approximately $10^{-9}$ m$^2$/sec at ambient conditions, and in most of the cases show weak functions of temperature and concentration. However, large variations in diffusivity values are often observed when one of the chemical species is a polymer or a macromolecule. The observed diffusion coefficients for polymer solvent systems cover a wide range of values and these coefficients can be strong functions of the temperature as well as concentration [Biesenberger, 1983].

The temperature dependence of diffusion coefficient for solvents in polymers does not usually follow a simple activation energy type correlation. In the conventional activation energy type correlation, a reciprocal of the absolute temperature yields a straight line whose slope is related to the activation energy for the diffusion process [Biesenberger, 1983]. As Figure 2.2 indicates, the apparent activation energy for polymer system can be a strong function of temperature, and large errors can be introduced by the usual extrapolation procedure.
Figure 2-3: Diffusion coefficient versus temperature diagram of methane-polystyrene and ethyl benzene-polystyrene systems [Bisenberger, 1983]
2.5 Research Objective

Molecular diffusion in polymer systems is a complex process which can be a strong function of concentration, temperature, polymer molecular weight and polymer morphology. Relatively few studies have been concerned with both concentration and temperature effects. Most of the data that are listed in Tables 2.1 to 2.3 have considered diffusivity as independent of concentration which is not the case [Duda 1978, '79, '82, ‘85]. As far as our research is concerned, there is no published data that show the concentration-dependence diffusivity of environmentally friendly gases like carbon dioxide and nitrogen in polymers. Emphasis will be placed on the description of molecular diffusion in a binary system consisting of polypropylene polymer and a low molecular weight solvent (such as carbon dioxide or nitrogen) at the limit of high polymer concentration. The influence of concentration and temperature on the molecular migration will be considered.
3 Experimentation

The experimental goal of this work was to measure pressure decay data of carbon dioxide and nitrogen gases in polypropylene at high temperatures and pressures, where the polypropylene is in a molten state. It was desired to determine the concentration dependent diffusivity of carbon dioxide and nitrogen gases in polypropylene melt at different temperatures and pressures. For this determination, it was necessary to obtain pressure decay data of the gases in polypropylene melt at experimental temperatures and pressures. Polypropylene having a weight average molecular weight \( M_w \) of 190,000 and number average molecular weight \( M_n \) of 50,000 was obtained from Sigma-Aldrich Canada Ltd. The melting point of polypropylene was 160–165°C and its melt index was 35.00. The gaseous solvents used in the experiments, nitrogen and carbon dioxide, had purity of 99.95%. These gases were received from British Oxygen Company Canada.
3.1 Pressure decay measurements

A pressure decay system was employed to determine concentration-dependent diffusivity of carbon dioxide and nitrogen in polypropylene. A constant volume pressure decay system measures the pressure drop of gas due to diffusion in polymer at constant temperature. The equilibrium pressure at sufficiently long time enables the calculation of solubility.

3.1.1 Experimental set-up

During this thesis work, a high pressure vessel was designed, constructed, tested and used to study the diffusion process of carbon dioxide and nitrogen gases in polypropylene melt at high pressures and different temperatures. Design considerations given by Koros and Paul [1976] were taken into account. Figures 3.1 and 3.2 show the schematic and picture of the stainless steel pressure vessel with a concentric 40 mm diameter cylindrical slot at the bottom to hold a polymer sample.
Figure 3-1: Schematic diagram of pressure vessel

Figure 3-2: Picture of pressure vessel

Viton® O-ring
Polypropylene Sample
Gas Entry
Pressure vessel lid
The lid of the pressure vessel had a glass window allowing a complete view of the polymer surface to online Keyence® LKG displacement laser sensor, which tracks the polymer surface movement with 10 micron accuracy. The lid was screwed to the vessel, and sealed using a Teflon core composite Viton® O-ring. Figure 3.3 shows a schematic diagram of experimental setup. As shown in figure, the pressure vessel was connected to a gas cylinder through a preheating coil and valves A and B. The gas cylinder was used for storing and pre-conditioning the gas obtained at the desired pressure by using a syringe pump [refer to Figure 3.4]. In order to maintain constant temperature condition (i.e., isothermal diffusion process) throughout the experiment, the whole experimental set-up was placed inside a forced convective oven with a temperature control of ±0.5°C.

In addition to the above-mentioned pressure vessel, Laser sensor, and oven, another main component in the experimental set-up is a high-precision Paroscientific Digiquartz® intelligent pressure transmitter which has a resolution of ±0.006 kPa and located between valves A and B to gather pressure verses time data. A vacuum pump was connected through valve C. Mounted outside the oven; the pressure transmitter and the laser sensor are connected to a computer data acquisition system. To prevent any kind of vibrations from the surroundings, the equipment was mounted on an air cushion. A photograph of the state-of-the-art experimental set-up for pressure decay is shown in Figure 3.5.
Figure 3-3: Schematic diagram of the experimental set-up
Figure 3-4: Photograph of syringe pump used to compress gas at desired pressure
Figure 3-5: Photograph of Experimental set-up for pressure decay system
3.1.2 Experimental Procedure

Prior to each experiment, the pressure vessel and all the connections were pressurized to 1.25 times the experimental pressure, to test for any kind of leakage. Gas cylinder valve and valve C were closed while valve B and A were open during the testing. After it was successful, valve C was opened, and polypropylene granules were placed in the sample slot to melt under vacuum at the experimental temperature, and form a cylindrical layer of uniform thickness. During the polymer heating to desired temperature vacuum was continuously applied to remove any kind of stagnant layer of air from the system. Having thus prepared the polypropylene sample, vacuum was applied to the whole system to check for any kind of leakage. After it was successful, valve C and A were closed and then after gas cylinder valve was opened. The gas was conditioned for 8 hrs. Then valve B was closed and valve A was opened to let the gas go through the area where we had pressure transmitter. By doing so we made sure that gas was properly heated to the desired temperature, and there were no further changes in pressure of gas. The laser sensor was then positioned and calibrated to track the distance from the polymer sample.

An experiment was started by quickly introducing the gas above the polymer surface inside the pressure vessel. This step was accomplished by simultaneously opening valve B and closing valve A to isolate the cell from the gasholder. As the introduced gas absorbed in the polymer phase, the system pressure decayed with time. The readings of the pressure transmitter and the laser sensor were recorded every 1.24 s until no reduction was detected. That is the time when the mass fraction of the gas in the polymer sample tends to a uniform equilibrium value. The experiment at that time was terminated, and valve C was gradually opened to release the gas. After the completion of each run, the polymer slot was cleaned up for the next run.
3.2 Summary of the Experiments

A detailed summary of all the pressure decay experiments is given in Table 3.1. For each solvent-polymer system, the data presented in this table include temperature, the initial pressure \( (P_i) \) i.e., the pressure at the start of the experiment, the final pressure \( (P_f) \) i.e., the equilibrium pressure of gas with polymer and pressure drop \( (\Delta P) \).

Figure 3.6 shows pressure decay data of carbon dioxide in polypropylene at initial pressure of 0.454 MPa 170\(^\circ\)C. For more pressure decay plots refer to Appendix A. This figure indicates that the pressure decays faster at the beginning of experimental run and finally tends to approach an asymptotic value i.e., the equilibrium pressure. Increasing the initial pressure at the same temperature, there is more pressure drop; it becomes obvious that the solubility of the gas increases with increase in pressure at the same temperature. On the other hand, increasing the temperature at the same pressure, there is less pressure drop this shows decrease in solubility. A larger pressure drop occurred when carbon dioxide was used compared to nitrogen at the same pressure and temperature [refer to Table 3.1]. This demonstrates that carbon dioxide has more solubility as compare to nitrogen. During experimental pressure decay, it took a long time for carbon dioxide to reach its complete saturation in polypropylene [refer to Appendix A]. This shows that carbon dioxide has lower diffusivity than nitrogen.
Table 3-1: Experimental Summary

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. (°C)</th>
<th>Initial Pressure ((P_i)) (MPa)</th>
<th>Final Pressure ((P_f)) (MPa)</th>
<th>Pressure Drop ((\Delta P)) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>170</td>
<td>0.454</td>
<td>0.426</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.350</td>
<td>2.190</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.710</td>
<td>3.470</td>
<td>0.240</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.770</td>
<td>6.450</td>
<td>0.320</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.291</td>
<td>0.277</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.990</td>
<td>0.927</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.856</td>
<td>1.740</td>
<td>0.116</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.785</td>
<td>2.623</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.100</td>
<td>3.870</td>
<td>0.230</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.430</td>
<td>5.166</td>
<td>0.264</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.780</td>
<td>6.490</td>
<td>0.290</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>1.425</td>
<td>1.344</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.670</td>
<td>2.543</td>
<td>0.127</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.450</td>
<td>5.232</td>
<td>0.218</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.320</td>
<td>7.029</td>
<td>0.291</td>
</tr>
<tr>
<td>N₂</td>
<td>170</td>
<td>0.994</td>
<td>0.972</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.977</td>
<td>2.902</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.110</td>
<td>3.029</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.170</td>
<td>4.049</td>
<td>0.121</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.400</td>
<td>5.264</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.733</td>
<td>0.722</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.256</td>
<td>1.234</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.987</td>
<td>1.950</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.124</td>
<td>2.084</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.090</td>
<td>3.025</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.917</td>
<td>3.827</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.753</td>
<td>6.592</td>
<td>0.161</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>2.000</td>
<td>1.974</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.110</td>
<td>3.055</td>
<td>0.055</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.310</td>
<td>4.222</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.350</td>
<td>5.230</td>
<td>0.120</td>
</tr>
</tbody>
</table>
Figure 3-6: Pressure decay plot of carbon dioxide in polypropylene at initial pressure of 0.454 MPa 170°C
3.3 Experimental Observations

The pressure decay plot [refer to Figure 3.6] indicates continuous pressure decay curves with decreasing value of pressure drop, which eventually becomes negligible and gives a equilibrium pressure at which the solubility of gas in polymer is obtained. As stated in experimental procedure [refer to sec. 3.1.2], the experiment was stopped when equilibrium was attained. Valve C was then opened slowly to depressurize the system.

Due to availability of a glass window on the top of the pressure vessel, depressurization of the polymer sample was visible. On observing this behavior carefully it was noticed that as we release the pressure, the absorbed gas inside the polymer melt starts making bubbles. As we had high pressure there was more pressure drop [refer to Figure 3.7] and there was more gas bubbles upon depressurization of system [refer to Figure 3.8]. To catch this stage, pressure vessel was quenched immediately after depressurization.
Figure 3-7: Experimental pressure drop of carbon dioxide gas at different pressures at 180°C

Figure 3-8: Sample after experimental runs at 180°C with Carbon dioxide
4 Theoretical Development

In this chapter the determination of gas diffusivity from the pressure decay experiments is presented as an optimal control problem [Upreti and Mehrotra, 2000]. For a given gas diffusivity, it is needed to calculate the mass of gas diffused in the polymer. To determine its experimental value, the experimental pressure decay data are utilized. To determine its model predicted value an appropriate mass transfer model is described. For some optimal gas diffusivity, the calculated and the experimental masses of the diffused gas would become equal. The conditions that are necessary for that optimality are derived.

4.1 Objective

It is desired to determine the diffusivity of gas as a function of its concentration in polymer melt from the experimental pressure decay data at a given temperature. Incorporating such a function in the mass transfer model of the experimental process, the calculated mass of gas diffused in polymer should be equal to its experimental value obtained from the experimentally recorded pressure data. An appropriate mass transfer model shall now be delineated for the experiments.

4.1.1 The mass transfer model

The unidirectional mass transfer model [refer to Figure 4.1] implements the law of conservation of mass i.e., the equation of continuity for gas that diffuses in polymer melt. Its underlying assumptions along with their justification are as follows:
✓ It's a unidirectional mass transfer model.

Since the polymer melt sample adheres to the pressure vessel base and the side walls, and one surface is exposed for the diffusion of gas, it can be assumed that diffusion through the polymer melt is unidirectional.

Figure 4-1: Unidirectional Mass transfers of gas in polymer melt

✓ There are no chemical reactions.

The absorption of gas in polymer melt is a purely physical phenomenon. Carbon dioxide and nitrogen are physical blowing agents that will not react with the polymer melt. This precludes any kind of chemical reaction.

✓ Mass transfer of gas in polymer melt is solely due to molecular diffusion. The system is at constant temperature. Any thermal energy released due to diffusion of gas is assumed to be dissipated instantaneously.

There was no vibrating equipment in the experimental set-up, which can make the chances of diffusion by bulk motion. To prevent any kind of external vibrations, the apparatus was placed on air cushion.
The concentration gradient is only along the depth of polymer melt i.e., $z$ direction. The wall effects are negligible.

To prevent any kind of wall effects the ratio of the depth of polymer melt to the internal diameter of pressure vessel was kept about 0.1 which is sufficiently low to neglect any wall effects.

All changes in pressure are only due to diffusion of gas in polymer melt.

The equipment was leak tested before the start of the run and there was no further pressure decay after the polymer melt sample become saturated with gas. This justifies that the equipment was leak proof and changes in pressure of gas was only due to diffusion in polymer melt.

4.1.1.1 The continuity equation

In the aforementioned experiments, the laser sensor did not detect any swelling of polymer melt due to gas diffusion at experimental temperatures and pressures. This may be due to very low solubility of gases in polymer melt; which has negligible effect on polymer melt density. Under the foregoing assumptions of mass transfer model, and by using Fick’s first law, the continuity equation for gas diffusing in polymer melt can be written as:

$$\frac{\partial \omega}{\partial t} = D \left[ 1 + \frac{\omega}{\rho} \right] \frac{\partial^2 \omega}{\partial z^2} + \left[ \left( 1 + \frac{\omega}{\rho} \right) \frac{\partial D}{\partial \omega} + \frac{D}{\rho} \right] \left( \frac{\partial \omega}{\partial z} \right)^2 \equiv f \quad (4.1)$$

The derivation of Equation (4.1) is given in Appendix B. In Equation 4.1, $\omega(z,t)$ is the mass concentration of gas in polymer melt at a depth $z$, and a time $t$. $D$ is the diffusivity of gas in
polymer melt, which depends on $\omega$. At constant temperature, this makes diffusivity a composite function, $D[\omega(z,t)]$.

### 4.1.1.2 Initial and boundary conditions

The specific solution of the above continuity equation depends upon the initial and boundary conditions. Before the start of the experiment i.e. at time $t=0$, the concentration of gas in polymer melt is equal to zero. Thus, the initial condition is given by:

$$\omega(z,0)=0 \quad \forall z : \quad 0 < z \leq L \quad (4.2)$$

At any time, at the bottom of the cell i.e. at $z = L$, the solid metal surface is impermeable to gas, which defines boundary condition as

$$\frac{\partial \omega}{\partial z} \bigg|_{z=L} = 0 \quad \forall t : \quad 0 \leq t \leq T \quad (4.3)$$

The interfacial concentration of gas is its equilibrium concentration, i.e. $\omega_{\text{sat}}$

$$\omega(0,t) = \omega_{\text{sat}}(t) \quad \forall t : \quad 0 \leq t \leq T \quad (4.4)$$

Equation 4.2 is the initial condition while Equations 4.3 and 4.4 are the boundary conditions for Equation 4.1. As value of $\omega_{\text{sat}}(t)$ which is the boundary condition for Equation (4.1) must be known before we solve Equation (4.1). This can be estimated from the experimental pressure decay data [refer to sec. 4.1.2].
4.1.2 The experimental mass of gas absorbed

The experimental mass of gas absorbed in the polymer melt is determinable from the experimentally recorded pressure versus time data, PVT data of carbon dioxide and nitrogen [Vargaftik et al., 1996], and by using cubic splines. Some of the PVT data of carbon dioxide and nitrogen obtained from Vargaftik et al.[1996] is presented in appendix C.

To determine mass of gas absorbed, PVT data of gases at different temperatures and pressures were used. At the start of solubility calculation, the specific volumes were plotted against pressures at different temperatures [refer to Figure 4.2]. We had taken eight data points but just to visualize we have shown three data points at three different temperatures in Figure 4.2. Then by using cubic spline interpolation at initial pressure of our experimental run, we can find specific volumes of gas at all temperatures. By doing so, we can find specific volumes of gas at different temperatures at initial pressure.

Furthermore, we will plot those specific volumes data points against different temperatures at the initial experimental pressure [refer to Figure 4.3], and by using cubic spline interpolation at the experimental temperature, we will have specific volume of gas at the initial pressure and experimental temperature. Same procedure can be repeated for final pressure of our experimental run. By doing this, will have specific volumes of gas at initial and final pressures of our experimental run. Using the value of system gas volume, and specific volumes at initial and final pressures, we can find out the solubility of gas in polymer at final pressure of the system.
For the solution of continuity equation we need to know the value of $\omega_{\text{sat}}(t)$, which is one of the boundary condition [refer to Equation 4.4]. That can be found by using the experimental solubility data. By plotting solubility against pressures and using cubic spline interpolation we can furnish our boundary condition of $\omega_{\text{sat}}(t)$. 
Figure 4-2: Cubic spline interpolations for PVT data of gases at experimental pressure

Figure 4-3: Cubic spline interpolations for PVT data of gases at experimental temperature
4.1.3 The objective functional

As stated earlier, the objective of this research is to minimize the difference between the mass of gas absorbed calculated from the experiment and mass of gas absorbed calculated through mass transfer model. The mathematical objective functional may be written as:

\[
I_{\min} = \int_0^T \left[ m_{gp,m}(t) - m_{gp,e}(t) \right]^2 dt
\]  

(4.5)

Where \( I_{\min} \) is the objective functional that needs to be minimized. At any time \( t \), \( m_{gp,e}(t) \) is the experimental mass of gas absorbed in the polymer while \( m_{gp,m}(t) \) is the model-predicted gas mass absorbed in polymer given by

\[
m_{gp,m}(t) = \int_0^L \omega(z,t)A dz
\]  

(4.6)

In the above equation, \( L \) is the depth of the polymer phase having a cross-sectional area \( A \). \( \omega(z,t) \) is the mass concentration of gas in polymer melt, which is a function of polymer melt depth and time \( t \). \( \omega(z,t) \) is obtained by the mass balance equation i.e. Equation (4.1) for a given but variable gas diffusivity that is an unknown function of \( \omega \) itself. Hence Equation (4.1) is the constraint for the minimization problem given by Equation (4.5). Equation (4.1) can also be written as:

\[
G(z,t) = \frac{\partial \omega}{\partial t} - f \left( \omega, \frac{\partial \omega}{\partial z}, \frac{\partial^2 \omega}{\partial z^2}, D \right)
\]  

(4.7)
The objective function given by Equation (4.5) is to be minimized taking into consideration the constraint represented by Equation (4.1). To convert this constrained optimization problem to unconstrained optimization problem an adjoint variable \( \lambda(z,t) \) is needed [Beveridge and Schechter, 1970]. By incorporating the adjoint variable \( \lambda(z,t) \) and constraint Equation (4.1) into objective function Equation (4.5) yields an augmented objective functional:

\[
F_{\text{min}} = \int_0^L \int_0^T \left[ I + \lambda(z,t)G(z,t) \right] \, dz \, dt
\]  

The minimization of \( F \) now becomes equivalent to the minimization of \( I \). The variational derivative of \( F \) with respect to the optimization variable \( D \) would provide the necessary condition for the minimum of \( F \) or \( I \).

### 4.1.3.1 The first variation of \( F \)

The first variation of \( F \) is required to derive the necessary optimality condition. This can be obtained as follows:

\[
\delta I = \frac{\partial I}{\partial \omega} (\delta \omega)
\]  

\[
\delta G = \frac{\partial}{\partial t} (\delta \omega) - \frac{\partial f}{\partial \omega} (\delta \omega) - \frac{\partial f}{\partial \omega_z} (\delta \omega_z) - \frac{\partial f}{\partial \omega_{zz}} (\delta \omega_{zz}) - \frac{\partial f}{\partial D} (\delta D)
\]

Where

\[
\omega_z = \frac{\partial \omega}{\partial z} \quad \text{and} \quad \omega_{zz} = \frac{\partial^2 \omega}{\partial z^2}
\]
By substituting Equations (4.9) and (4.10) into Equation (4.8) yields the following Variation

$$\delta F = \int_0^L \int_0^L \left[ \left( \frac{\partial I}{\partial \omega} - \lambda \frac{\partial f}{\partial \omega} \right) \delta \omega + \lambda \left( \frac{\partial (\delta \omega)}{\partial t} - \frac{\partial f}{\partial \omega_z}(\delta \omega_z) - \frac{\partial f}{\partial \omega_{zz}}(\delta \omega_{zz}) - \frac{\partial f}{\partial D}(\delta D) \right) \right] dz dt$$

(4.12)

Integration by parts of the third, fourth, and fifth term on right hand side in Equation (4.12) yields the following equations:

$$\int_0^L \int_0^L \lambda \frac{\partial (\delta \omega)}{\partial t} dz dt = \int_0^L \int_0^L \left[ \frac{\partial \lambda}{\partial \omega} \delta \omega \right]_0^L - \int_0^L \frac{\partial \lambda}{\partial \omega} \delta \omega dt$$

(4.13)

$$\int_0^L \int_0^L \lambda \frac{\partial f}{\partial \omega_z} \delta \omega_z dz dt = \int_0^L \int_0^L \left[ \frac{\partial \lambda}{\partial \omega_z} \delta \omega_z \right]_0^L - \int_0^L \frac{\partial \lambda}{\partial \omega_z} \delta \omega_z dt$$

(4.14)

$$\int_0^L \int_0^L \lambda \frac{\partial f}{\partial \omega_{zz}} \delta \omega_{zz} dz dt = \int_0^L \int_0^L \left[ \frac{\partial \lambda}{\partial \omega_{zz}} \frac{\partial (\delta \omega)}{\partial z} - \frac{\partial \lambda}{\partial \omega_{zz}} \frac{\partial (\delta \omega_{zz})}{\partial z} \right]_0^L$$

$$+ \int_0^L \frac{\partial^2 \lambda}{\partial z^2} \delta \omega_{zz} dt$$

(4.15)
Substitution of Equations (4.13)–(4.15) into Equation (4.12) gives:

\[
\delta F = \int_0^L \left[ - \frac{\partial \lambda}{\partial t} + \frac{\partial I}{\partial \omega} - \lambda \frac{\partial f}{\partial \omega} + \frac{\partial}{\partial z} \left( \lambda \frac{\partial f}{\partial \omega_z} \right) - \frac{\partial^2}{\partial z^2} \left( \lambda \frac{\partial f}{\partial \omega_{zz}} \right) \right] \delta \omega dz \, dt
\]

\[
- \int_0^L \lambda \frac{\partial f}{\partial \omega_z} \delta Dz \, dt + \int_0^L \left[ \lambda \delta \omega \right] \delta Dz + \int_0^L \left[ \frac{\lambda}{\partial \omega_z} - \frac{\partial}{\partial z} \left( \lambda \frac{\partial f}{\partial \omega_{zz}} \right) \right] \delta \omega (0,t) \, dt \]

\[
- \int_0^L \left[ \lambda \frac{\partial f}{\partial \omega_z} - \frac{\partial}{\partial z} \left( \lambda \frac{\partial f}{\partial \omega_{zz}} \right) \right] \delta \omega (L,t) \, dt - \int_0^L \left[ \lambda \frac{\partial f}{\partial \omega_{zz}} \frac{\partial}{\partial \omega} (\delta \omega) \right] \delta \omega \, dt = 0
\]

(4.16)

In the above equation, the first term is eliminated by defining \( \lambda \) as

\[
\frac{\partial \lambda}{\partial t} = \frac{\partial I}{\partial \omega} - \lambda \frac{\partial f}{\partial \omega} + \frac{\partial}{\partial z} \left( \lambda \frac{\partial f}{\partial \omega_z} \right) - \frac{\partial^2}{\partial z^2} \left( \lambda \frac{\partial f}{\partial \omega_{zz}} \right)
\]

(4.17)

The above equation 4.17 has the following final form:

\[
\frac{\partial \lambda}{\partial t} = 2A \left( m_{gp,m} - m_{gp,e} \right) + \lambda \frac{\partial D}{\partial \omega} \left( \frac{\partial \omega}{\partial z} \right)^2 + \left( 1 + \frac{\omega}{\rho} \right) \left[ \lambda \frac{\partial D}{\partial \omega} \left( \frac{\partial \omega}{\partial z} \right)^2 + \lambda \frac{\partial^2 D}{\partial \omega^2} \left( \frac{\partial \omega}{\partial z} \right)^2 - D \frac{\partial^2 \lambda}{\partial z^2} \right]
\]

(4.18)

Equation (4.18) is called the adjoint equation.
Because the initial mass concentration of the gas in the polymer is known at the interface and is zero elsewhere, the variation $\delta \omega(z,0)$ is zero for all $z$. Since the final mass concentration is not specified, the third integral in Equation (4.16) is eliminated by forcing

$$\lambda(z,T) = 0 \quad 0 \leq z \leq L$$

(4.19)

Since the equilibrium concentration of gas at the interface, $\omega(0,t) = \omega_{\text{sat}}(t)$, is always specified $\delta \omega(0,t)$ is zero. Thus, the fourth term is also eliminated in Equation (4.16). Furthermore, by forcing

$$\lambda(L,t) = 0 \quad 0 \leq t \leq T$$

(4.20)

the fifth integral in Equation (4.16) is eliminated. In addition by setting

$$\lambda(0,t) = 0 \quad 0 \leq t \leq T$$

(4.21)

eliminates the sixth integral in Equation (4.16). Equations (4.20) and (4.21) are the boundary conditions, and Equation (4.19) is the initial condition at final time for adjoint equation i.e., Equation (4.18).

Subjected to Equations (4.17)–(4.21), Equation (4.16) can be simplified to:

$$\delta F = -\int_0^T \int_0^L \lambda \frac{\partial f}{\partial D} \delta D dz dt = 0$$

(4.22)

Thus, at the minimum, the first variational derivative of $F$ given by Equation (4.22) is zero.
That is only possible when

\[- \lambda \frac{\partial f}{\partial D} = 0 \quad 0 \leq z \leq L, \quad 0 \leq t \leq T \quad (4.23)\]

Thus, Equation (4.23) is the necessary condition for the minimization of \( F \) or equivalently of \( I \) when the continuity as well as adjoint equations, i.e., Equations (4.1) and (4.18) are satisfied. These equations can be solved using finite difference method.

### 4.1.4 Finite difference form of continuity equation

The finite difference form of continuity equation at each grid point is

\[
\frac{d\omega_i}{dt} = D(\omega_i) \left[ 1 + \frac{\omega_i}{\rho} \left( \frac{\omega_{i-1} - 2\omega_i + \omega_{i+1}}{\Delta z^2} \right) + \left( 1 + \frac{\omega_i}{\rho} \right) \frac{dD}{d\omega} + \frac{D(\omega_i)}{\rho} \left( \frac{\omega_i}{2z} \right)^2 \right]
\]

\[
\forall i: \ 1 < i < N
\]

\[
\frac{d\omega_N}{dt} = 2D(\omega_N) \left[ 1 + \frac{\omega_N}{\rho} \left( \frac{\omega_{N-1} - \omega_N}{\Delta z^2} \right) \right]
\]

In Equation (4.24), \( D \) is the diffusivity of gas in polymer, \( \omega_{\text{sat}} \) is the saturated interfacial mass concentration and \( \omega_i \) is the mass concentration of gas at the \( i \)-th grid point.
4.1.5 Finite difference form of adjoint equation

Similarly the final difference form of adjoint equation is

\[
\frac{d\lambda_i}{dt} = 0
\]

\[
\frac{d\lambda_i}{dt} = 2A(m_{gp,m} - m_{gp,e}) + \frac{\lambda}{\rho} \frac{dD}{d\omega_i} \left( \frac{\omega_{i+1} - \omega_{i-1}}{2z} \right)^2 + \left( 1 + \frac{\omega_i}{\rho} \right) \left[ \lambda \frac{dD}{d\omega_i} \left( \frac{\omega_{i+1} - 2\omega_i + \omega_{i-1}}{\Delta z^2} \right) + \right]

\left[ \frac{\lambda}{\rho} \frac{dD}{d\omega_i} \left( \frac{\omega_{i+1} - 2\omega_i + \omega_{i-1}}{\Delta z^2} \right) \right]

\forall i: 1 < i < N

\[
\frac{d\lambda_N}{dt} = 0
\]

In Equation (4.25), \( \lambda_i \) is the value of adjoint variable at the \( i \)-th grid point, \( m_{gp,m} \) and \( m_{gp,e} \) are mass of gas in polymer by model and mass of gas in polymer by experiment respectively.
4.1.6 Solution methodology for diffusivity calculation

Due to the presence of highly non-linear partial differential equations, the analytical solution of this optimization problem was not possible. Therefore, the problem had to be solved numerically. To start the solution of the problem, an initial guess for diffusivity was provided and the continuity equation i.e., Equation (4.1) was solved forward along time domain to obtain the value of $\omega$ at each node with respect to time i.e., $\omega(z,t)$ [refer to Figure 4.4]. A total number of sixty nodes were used in the calculation. No further improvement in the objective function was observed after sixty nodes. Those values of $\omega$ were stored for the solution of adjoint equation i.e., Equation (4.25). As adjoint equation had initial condition at final time [refer to Equation (4.19)], the adjoint equation was solved backward along the time domain by using values of $\omega(z,t)$ to get the value of $\lambda$ at each node with respect to time i.e., $\lambda(z,t)$. These values of $\lambda(z,t)$ were used for the calculation of necessary condition i.e., Equation (4.23). The negative of this necessary condition provided the steepest descent direction for the optimization problem. By doing this iterative procedure we had the value of modified diffusivity i.e., $D_{mod}$, and that value of modified diffusivity was used to replace the initial diffusivity guess. This iterative procedure was continued until there was no further improvement in objective function [refer to Figure 4.5].
Figure 4-4: Solution methodology for diffusivity calculation
Figure 4-5: Extent of minimization of objective function
5 Results and Discussion

This chapter presents the concentration dependent diffusivity as well as solubility of carbon dioxide and nitrogen in polypropylene at various temperatures and pressures. The results presented here are in the range of 170–190°C and 0.29–7.32 MPa. A mathematical correlation for diffusivity calculation has been provided in this chapter.

5.1 Results for Carbon Dioxide

Figures 5.1–5.3 shows the concentration dependent diffusivity behavior of carbon dioxide in polypropylene at different temperatures and pressures. At a given pressure and temperature, the diffusivity of carbon dioxide increases with its concentration in polypropylene and then decreases towards the end as the polymer sample moves closer to its saturation concentration. This can be explained on the basis that, at the start of the diffusion a small diffusion of gas molecule increases the free volume of the mixture. This will consequently increase the diffusion coefficient with the solvent concentration and it will reach a maximum value. After that it will start decreasing, because the whole free volume of the matrix will be filled up with the gas molecules and it will start approaching its saturation limit due to which the diffusivity will decrease. In this work, the carbon dioxide peak diffusivity in polypropylene at the experimental temperatures and pressures is found to lie between 2.67–9.13×10⁻⁹ m² s⁻¹. The peak diffusivity values at each experimental temperature and pressure are provided in Table 5.1.
Figure 5-1: Concentration dependent diffusivity of carbon dioxide in polypropylene at various pressures at 170°C
Figure 5-2: Concentration dependent diffusivity of carbon dioxide in polypropylene at different pressures at 180°C
Figure 5-3: Concentration dependent diffusivity of carbon dioxide in polypropylene at different pressures at 190°C
Table 5-1: Peak diffusivity values of carbon dioxide in polypropylene at experimental temperatures and pressures.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (MPa)</th>
<th>Peak Diffusivity $\times 10^9$ (m$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>0.45</td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td>3.71</td>
<td>4.67</td>
</tr>
<tr>
<td></td>
<td>6.77</td>
<td>3.27</td>
</tr>
<tr>
<td>180</td>
<td>0.29</td>
<td>2.67</td>
</tr>
<tr>
<td></td>
<td>0.99</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>4.01</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>4.09</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td>5.43</td>
<td>3.46</td>
</tr>
<tr>
<td></td>
<td>6.78</td>
<td>3.48</td>
</tr>
<tr>
<td>190</td>
<td>1.44</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td>2.67</td>
<td>7.10</td>
</tr>
<tr>
<td></td>
<td>5.45</td>
<td>7.85</td>
</tr>
<tr>
<td></td>
<td>7.32</td>
<td>9.13</td>
</tr>
</tbody>
</table>
5.2 Results for Nitrogen

Figures 5.4–5.6 shows the concentration dependent diffusivity behavior of nitrogen in polypropylene at different temperatures and pressures. At a given pressure and temperature, the diffusivity of nitrogen increases with its concentration in polypropylene and then decreases towards the end as the polymer sample moves closer to its saturation concentration. This can be explained on the basis as discussed in section 5.1 for carbon dioxide. In this work, the nitrogen peak diffusivity in polypropylene at the above mentioned temperature and pressure is found to lie between $3.88 \times 10^{-9}$ $m^2 s^{-1}$. The peak diffusivity values at each experimental temperatures and pressures are provided in Table 5.2. The diffusion coefficient of nitrogen in polypropylene is of the same order of magnitude as that determined by Durill and Griskey [1966], and Sato et al. [1999].
Figure 5-4: Concentration dependent diffusivity of nitrogen in polypropylene at different pressures at 170°C.
Figure 5-5: Concentration dependent diffusivity of nitrogen in polypropylene at different pressures at 180°C
Figure 5-6: Concentration dependent diffusivity of nitrogen in polypropylene at different pressures at 190°C
Table 5-2: Peak diffusivity values of nitrogen in polypropylene at experimental temperatures and pressures.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (MPa)</th>
<th>Peak Diffusivity × 10⁹ (m² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>0.99</td>
<td>4.08</td>
</tr>
<tr>
<td></td>
<td>2.98</td>
<td>4.22</td>
</tr>
<tr>
<td></td>
<td>3.11</td>
<td>4.51</td>
</tr>
<tr>
<td></td>
<td>4.17</td>
<td>11.20</td>
</tr>
<tr>
<td></td>
<td>5.40</td>
<td>12.94</td>
</tr>
<tr>
<td>180</td>
<td>0.73</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td>1.26</td>
<td>6.45</td>
</tr>
<tr>
<td></td>
<td>1.99</td>
<td>5.90</td>
</tr>
<tr>
<td></td>
<td>2.12</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>3.09</td>
<td>7.63</td>
</tr>
<tr>
<td></td>
<td>3.92</td>
<td>6.42</td>
</tr>
<tr>
<td></td>
<td>6.75</td>
<td>11.33</td>
</tr>
<tr>
<td>190</td>
<td>2.00</td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td>3.11</td>
<td>10.90</td>
</tr>
<tr>
<td></td>
<td>4.31</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>5.35</td>
<td>12.13</td>
</tr>
</tbody>
</table>
5.3 Temperature effect on diffusivity

The several temperatures used in this study (170°C, 180°C, and 190°C) were selected to provide significant variation of the diffusion coefficient. No temperature higher than 190°C was used because of the O-ring degradation. Figures 5.7 and 5.8 demonstrate the effect of temperature on molecular diffusion of gases. It is immediately obvious that the diffusion is a temperature sensitive parameter. At a given pressure, the diffusivity of gases in polypropylene increase with temperature. This can be attributes to the following reasons:

- As the temperature of the melt increases the viscosity will decrease and if there is less viscosity the molecule can travel easily through the polymer melt which increases the diffusivity of the solvent.
- The activation energy of gas will be larger at lower temperature and as we increase the temperature the activation energy will decrease which will increase diffusivity.
- The increase in temperature increases the molecular motion of the polymer, allowing the gas to penetrate the polymer matrix more easily.

The temperature dependence of diffusion coefficient for this system is typically the same as observed for other polymer solvent system [Rehage et al. 1970, Tendulkar 2007, Duda 1973, ‘78, ‘79, and ‘82].
Figure 5-7: Temperature effect on diffusivity of nitrogen in polypropylene
Figure 5-8: Temperature effect on diffusivity of carbon dioxide in polypropylene
5.4 Pressure effect on diffusivity

Figures 5.1–5.6 indicate the effect of pressure at experimental temperatures (170°C, 180°C, and 190°C) on diffusivity of carbon dioxide and nitrogen respectively. As can be observed the effect of pressure on diffusivity is complex. Increase in pressure increases the frequency of intermolecular collisions, but reduces the intermolecular distances. While increased molecular collision facilitates gas diffusion, the reduces intermolecular distances impedes it. Thus, at a given pressure, depending on the dominance of first or second effect, the peak diffusivity increases or decreases respectively with pressure. This pressure dependence of diffusion coefficient for this system is typically the same as observed for other polymer solvent system [Robert 2000, and Tendulkar 2007].

5.5 Solubility of Gases

The solubility of carbon dioxide and nitrogen in polypropylene was measured at three different temperatures (170°C, 180°C, and 190°C) and pressure up to 7.32 MPa. Figure 5.9 and 5.10 shows the solubility of carbon dioxide and nitrogen in polypropylene respectively. Solubility values at experimental temperatures and pressures are provided in Appendix D. At a given pressure, solubility of both gases decrease with increase in temperature. At a given temperature, the solubility of both gases increases with increase in pressure. This temperature and pressure dependence of solubility is usually observed in gases and polymer system [Sato et al. 2001, Tendulkar 2007].

It should be emphasized at this point that by increase in temperature there will be decrease in solubility caused by the decrease in surface concentration. On the other hand, as pressure
control the number of gas molecule collisions with surface of the melt, the increase number of collisions produce more dissolved gas. The solubility data of this work is compared with the data generated by Sato et al. [1999] [refer to Figure 5.10]. There is small discrepancy in results. This could be attributed to nature and magnitude of polymer-penetrant interactions, as well as on the distribution of shapes, and sizes of open spaces formed among the chains within the polymer, where penetrant molecules can reside.

The solubility of carbon dioxide has been compared with nitrogen at experimental temperatures and pressures [refer to Figure 5.11]. As can be observed, at the same temperatures and pressures carbon dioxide has more solubility in polypropylene as compare to nitrogen. This behavior can also be observed in pressure decay diagram [refer to Appendix A], where at the same temperature and pressure carbon dioxide has more pressure drop as compare to nitrogen.
Figure 5-9: Solubility of carbon dioxide in polypropylene at different temperatures.
Figure 5-10: Solubility of nitrogen in polypropylene at different temperatures.
Figure 5-11: Comparison of solubility of carbon dioxide with nitrogen in polypropylene at experimental temperatures and pressures.
5.6 The sensitivity analysis

As indicated in Figures 5.12 and 5.13, sensitivity analysis for both gases was carried out to determine the effect of change in system volume on diffusivity. It compares the diffusivity value at actual volume to ±2% variations. These variations conservatively embody the maximum possible error in the system volume. As observed from the figures, the three graphs overlap. In fact, the average of the changes in diffusivity is less than 0.06%.

Figure 5-12: Sensitivity analysis to gas volume change of carbon dioxide gas at 0.29 MPa 180°C
Figure 5-13: Sensitivity analysis to gas volume change of nitrogen gas at 1.85 MPa 180°C
5.7 Summary of the Results

5.7.1 Diffusivity

The diffusivity results for both the gases CO₂ and N₂ presented in Figures 5.1–5.6 clearly show that the diffusivity of a gas in a polymer is a function of concentration. The diffusivity of the gas in polymer increases with its concentration to a maximum value and then decreases subsequently. This result is expected and can be explained on the basis that, at the start of the diffusion a small diffusion of gas molecule which has more free volume as compare to polymer matrix enhance the free volume of the mixture. This will consequently increase the diffusion coefficient with the solvent concentration and it will reach a maximum value. After that it will start decreasing, because the whole free volume of the matrix will be filled up with the gas molecules and it will start approaching its saturation limit due to which the diffusivity will decrease. This diffusivity effect can be observed in pressure decay diagram [refer to Appendix A], where there is more pressure decay at the start of the experimental run and later on which decreases and approach a constant value.

At a given pressure, the diffusivity of both gases in polymer increases with increase in temperature. This can be attributed to decrease in melt viscosity, decrease in activation energy and increase in molecular motion, allowing the gas to penetrate the polymer matrix more easily.

The effect of pressure on the diffusion coefficient appears to be much less pronounced. Although Increase in pressure increases the frequency of intermolecular collisions, but at the same time it reduces the intermolecular distances. While increased molecular collision facilitates gas diffusion, the reduced intermolecular distance impedes it. Therefore, when gas
diffusivity increases with pressure, the increased frequency of molecular collisions has a dominating effect. Thus, at a given pressure, depending on the dominance of first or second effect, the peak diffusivity increases or decreases respectively with pressure.

At the same temperature and pressure nitrogen has larger diffusivity as compare to carbon dioxide. This behavior can be observed in pressure decay diagram [refer to Appendix A], where it can be observed that at the same temperature and pressure nitrogen require less time to reach its saturation concentration as compare to carbon dioxide. It is generally accepted picture of the mechanism of the diffusion process that larger holes needed to be formed in the polymer for the diffusion of larger molecules. These will require a larger energy for their formation and hence activation energy will be larger for the diffusion of bigger molecules (Carbon dioxide) as compare to smaller molecules (Nitrogen) and the diffusivity will be smaller.

5.7.2 Solubility

At a given temperature, the solubility increases with increase in pressure. This can be attributed to increase in number of collision of gas molecule to the surface of polymer melt which will increase solubility. The solubility of nitrogen in polypropylene was found to be smaller than carbon dioxide. This behavior can be observed during experimental run at the same temperature and pressure where nitrogen has less pressure drop as compare to carbon dioxide [refer to Appendix A]. It is observed that with the increase in temperature the solubility of both gases decreases.
5.8 Mathematical correlation for diffusivity

The diffusivity versus concentration data obtained in this work was mathematically correlated to obtain the diffusivity as a function of concentration and pressure at a given temperature. For this purpose, TCD3D™ was utilized to find the best fitting for diffusivity as a concentration and pressure. That function is as follows:

\[ D = a_0 + a_1 \ln P + a_2 \ln \omega + a_3 (\ln P)^2 + a_4 (\ln \omega)^2 + a_5 \ln P \ln \omega + a_6 (\ln P)^3 + a_7 (\ln \omega)^3 + a_8 (\ln P)^2 + a_9 (\ln P)^3 \ln(\omega) \] (5.1)

Table 5.3 and 5.4 list the fitting parameters \([a_0 \text{ through } a_9]\) values and detail of Equation 5.1 for carbon dioxide and nitrogen respectively.

Table 5-3: Parameters for mathematical correlation Equation (5.1) at different temperatures for carbon dioxide gas

<table>
<thead>
<tr>
<th>Temperatures</th>
<th>170°C</th>
<th>180°C</th>
<th>190°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_0)</td>
<td>4.869</td>
<td>3.866</td>
<td>1.527</td>
</tr>
<tr>
<td>(a_1)</td>
<td>-6.431</td>
<td>0.168</td>
<td>13.468</td>
</tr>
<tr>
<td>(a_2)</td>
<td>-0.028</td>
<td>-0.234</td>
<td>-0.620</td>
</tr>
<tr>
<td>(a_3)</td>
<td>8.457</td>
<td>-0.785</td>
<td>-10.898</td>
</tr>
<tr>
<td>(a_4)</td>
<td>-0.324</td>
<td>-0.299</td>
<td>-0.709</td>
</tr>
<tr>
<td>(a_5)</td>
<td>0.493</td>
<td>0.561</td>
<td>1.115</td>
</tr>
<tr>
<td>(a_6)</td>
<td>-2.980</td>
<td>0.223</td>
<td>2.897</td>
</tr>
<tr>
<td>(a_7)</td>
<td>-0.001</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>(a_8)</td>
<td>0.001</td>
<td>0.008</td>
<td>0.002</td>
</tr>
<tr>
<td>(a_9)</td>
<td>-0.001</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.93</td>
<td>0.87</td>
<td>0.93</td>
</tr>
</tbody>
</table>
Table 5-4: Parameters for mathematical correlation Equation (5.1) at different temperatures for nitrogen gas

<table>
<thead>
<tr>
<th>Parameters</th>
<th>170°C</th>
<th>180°C</th>
<th>190°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>1.821</td>
<td>3.222</td>
<td>-133.352</td>
</tr>
<tr>
<td>$a_1$</td>
<td>-41.995</td>
<td>5.433</td>
<td>391.470</td>
</tr>
<tr>
<td>$a_2$</td>
<td>-2.671</td>
<td>-2.219</td>
<td>-4.344</td>
</tr>
<tr>
<td>$a_3$</td>
<td>62.058</td>
<td>-6.580</td>
<td>-342.662</td>
</tr>
<tr>
<td>$a_4$</td>
<td>-0.745</td>
<td>-0.483</td>
<td>-0.943</td>
</tr>
<tr>
<td>$a_5$</td>
<td>1.392</td>
<td>0.967</td>
<td>2.170</td>
</tr>
<tr>
<td>$a_6$</td>
<td>-19.871</td>
<td>3.027</td>
<td>95.879</td>
</tr>
<tr>
<td>$a_7$</td>
<td>-0.001</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>$a_8$</td>
<td>-0.002</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>$a_9$</td>
<td>0.004</td>
<td>-0.001</td>
<td>-0.001</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.96</td>
<td>0.92</td>
<td>0.95</td>
</tr>
</tbody>
</table>
6 Conclusions and Recommendations

6.1 Conclusions

The diffusivity data obtained in this work are the first which show the concentration dependent diffusivity of carbon dioxide and nitrogen in polypropylene. These data were experimentally determined at temperatures 170°C, 180°C, and 190°C, and 0.45–7.32 MPa.

The diffusivity of CO₂ and N₂ gases is a function of gas concentration in polymer. At a given pressure, diffusivity increases with temperature. Nitrogen has larger diffusivity in polypropylene as compare to carbon dioxide. This confirms the commonly accepted viewpoint that the size of the diffusing molecule is the primary factor in determining the rate of diffusion and that the thermodynamic interaction between the polymer and the penetrant is relatively unimportant.

The values of the diffusion coefficient of N₂ gas reported here (3.88–12.94 x 10⁻⁹ m² s⁻¹) are of similar order of magnitude as those reported by earlier investigators.

For both gases considered in this work, at a given pressure, the solubility decreases with increase in temperature. At a given temperature, the solubility of both gases increases with increase in pressure. This temperature and pressure dependence of solubility is usually observed in gases and polymer system. Carbon dioxide is more soluble in polypropylene as compare to nitrogen.
6.2 Recommendations for further work

The pressure decay technique has wide applications in the investigation of concentration dependent diffusivity of gases in polymers. However, for polymers with higher melting points, there is a limitation due to the maximum operating temperature of Viton® O-ring. To generate concentration dependent diffusivity data, a suitable o-ring for high temperature conditions is needed.

It can be argued that there will be a different diffusion rates of gases in lower molecular weight distribution polymer (MWD) compared to higher molecular weight distribution polymers. The best test is to use different molecular weights polymer and find the effect of molecular weight distribution on diffusion rate.

It is recommended that a study be done similar to the one presented here at higher pressures. To conduct higher pressure study, there is a need to change the glass cover of the pressure vessel. For higher pressure we need more pressure resistant glasses. This means we need to redesign the pressure vessel. A robust piping system will moreover be needed to operate at high temperature and pressure.

The present study is focused towards understanding the diffusion of gases in homogeneous polymer. It will be of great interest to extend the work to study diffusion of gases in copolymer systems and results can be used in understanding systems of practical interest with predetermined heterogeneity.
References


APPENDIX A

PRESSURE DECAY PLOTS

A constant volume pressure decay system was employed to measure the pressure decay of gas due to diffusion in polymer at constant temperature. The pressure transducer which has resolution of ±0.006 kPa was used to measure pressure drop at every 1.24 s until no reduction was detectible. Figure A-1 to A-25 shows the pressure decay plots of both gases (CO₂ and N₂), at experimental temperatures and pressures.

Figure A-1: Pressure decay plot of carbon dioxide at 1.440 MPa 170°C
Figure A-2: Pressure decay plot of carbon dioxide at 2.350 MPa 170°C

Figure A-3: Pressure decay plot of carbon dioxide at 3.710 MPa 170°C
Figure A-4: Pressure decay plot of carbon dioxide at 6.770 MPa 170°C

Figure A-5: Pressure decay plot of carbon dioxide at 0.291 MPa 180°C
Figure A-6: Pressure decay plot of carbon dioxide at 0.990 MPa 180°C

Figure A-7: Pressure decay plot of carbon dioxide at 1.856 MPa 180°C
Figure A-8: Pressure decay plot of carbon dioxide at 2.785 MPa 180°C

Figure A-9: Pressure decay plot of carbon dioxide at 4.100 MPa 180°C
Figure A-10: Pressure decay plot of carbon dioxide at 5.430 MPa 180°C

Figure A-11: Pressure decay plot of carbon dioxide at 6.780 MPa 180°C
Figure A-12: Pressure decay plot of carbon dioxide at 1.425 MPa 190°C

Figure A-13: Pressure decay plot of carbon dioxide at 2.670 MPa 190°C
Figure A-14: Pressure decay plot of carbon dioxide at 5.450 MPa 190°C

Figure A-15: Pressure decay plot of nitrogen at 0.994 MPa 170°C
Figure A-16: Pressure decay plot of nitrogen at 2.977 MPa 170°C

Figure A-17: Pressure decay plot of nitrogen at 0.733 MPa 180°C
Figure A-18: Pressure decay plot of nitrogen at 1.256 MPa 180°C

Figure A-19: Pressure decay plot of nitrogen at 1.987 MPa 180°C
Figure A-20: Pressure decay plot of nitrogen at 2.124 MPa 180°C

Figure A-21: Pressure decay plot of nitrogen at 3.090 MPa 180°C
Figure A-22: Pressure decay plot of nitrogen at 6.753 MPa 180°C

Figure A-23: Pressure decay plot of nitrogen at 2.009 MPa 190°C
Figure A-24: Pressure decay plot of nitrogen at 4.310 MPa 190°C

Figure A-25: Pressure decay plot of nitrogen at 5.350 MPa 190°C
APPENDIX B

EQUATION OF CONTINUITY

For the one dimensional transient diffusion of a gas in polymer, the mass balance in the polymer layer is:

\[ \frac{\partial \omega}{\partial t} + \frac{\partial N}{\partial z} = 0 \]  \hspace{1cm} (A.1)

The molar flux of gas in a stationary layer of Polymer is

\[ N = x(N + 0) + J \]  \hspace{1cm} (A.2)

In Equation (A.2), the first term on right hand side represents the mass flux of gas in the polymer resulting from the bulk motion and second term on right hand side represents the mass flux of gas resulting from diffusion superimposed on the bulk flow.

There diffusive mass flux \( J \) of gas in polymer is given by:

\[ J = -D \frac{\partial \omega}{\partial z} \]  \hspace{1cm} (A.3)

This is the Fick’s law of diffusion. By substituting the value of \( J \) into Equation (A.2), we will get:

\[ N = xN - D \frac{\partial \omega}{\partial z} \]  \hspace{1cm} (A.4)
This gives
\[ N = \frac{-D}{(1-x)} \frac{\partial \omega}{\partial z} \]  
\hspace{10cm} (A.5)

By substituting the value of \( N \) into Equation (A.1), we will get

\[ \frac{\partial \omega}{\partial t} + \frac{\partial}{\partial z} \left[ \frac{-D}{(1-x)} \frac{\partial \omega}{\partial z} \right] = 0 \]  
\hspace{10cm} (A.6)

Where \( x = \frac{\omega}{\omega + \rho} \) \hspace{10cm} (A.7)

By substituting the value of \( x \) in Equation A.6 and solving further we will get

\[ \frac{\partial \omega}{\partial t} = D \left( 1 + \frac{\omega}{\rho} \right) \frac{\partial^2 \omega}{\partial z^2} + \left[ \left( 1 + \frac{\omega}{\rho} \right) \frac{\partial D}{\partial \omega} + \frac{D}{\rho} \right] \left( \frac{\partial \omega}{\partial z} \right)^2 \]
APPENDIX C

PVT Data of Carbon Dioxide and Nitrogen

To determine the experimental mass of gas absorbed from recorded pressure versus time data, PVT data of both gases (carbon dioxide and nitrogen) was required. PVT data of both gases was obtained from Vargaftik et al. [1996]. Table C-1 and C-2 shows some of the PVT data of carbon dioxide and nitrogen respectively.

Table C-1: Specific volume of Carbon dioxide at different temperatures and pressures

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure (MPa)</th>
<th>Specific Volume (m³/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>166.85 °C</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.10</td>
<td>830.20</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>414.60</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>206.80</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>137.50</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>102.90</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>82.07</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>54.61</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>40.52</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>32.21</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>26.67</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
<td>22.71</td>
</tr>
<tr>
<td></td>
<td>4.00</td>
<td>19.75</td>
</tr>
<tr>
<td></td>
<td>4.50</td>
<td>17.44</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>15.60</td>
</tr>
<tr>
<td></td>
<td>5.50</td>
<td>14.09</td>
</tr>
<tr>
<td></td>
<td>6.00</td>
<td>12.83</td>
</tr>
<tr>
<td></td>
<td>6.50</td>
<td>11.77</td>
</tr>
<tr>
<td></td>
<td>7.00</td>
<td>10.86</td>
</tr>
<tr>
<td></td>
<td>7.50</td>
<td>10.07</td>
</tr>
<tr>
<td></td>
<td>8.00</td>
<td>9.39</td>
</tr>
<tr>
<td></td>
<td>9.00</td>
<td>8.24</td>
</tr>
</tbody>
</table>
Table C-2: Specific volume of Nitrogen at different temperatures and pressures

<table>
<thead>
<tr>
<th>Gas</th>
<th>Pressure (MPa)</th>
<th>Specific Volume (m³/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>76.85 °C</td>
<td>126.85 °C</td>
</tr>
<tr>
<td>N₂</td>
<td>0.10</td>
<td>1.038</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.207</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.104</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>4.00</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>15.00</td>
<td>0.007</td>
</tr>
</tbody>
</table>
# APPENDIX D

**Table D-1:** Solubility data of Carbon dioxide and Nitrogen in polypropylene at experimental temperatures and pressures.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. (°C)</th>
<th>Pressure (MPa)</th>
<th>Solubility × 10³ (kg-gas / kg-polymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>170</td>
<td>0.43</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.34</td>
<td>7.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.19</td>
<td>13.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.48</td>
<td>20.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.45</td>
<td>29.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.28</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>0.93</td>
<td>4.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.74</td>
<td>8.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.42</td>
<td>12.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.62</td>
<td>13.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.85</td>
<td>14.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.87</td>
<td>18.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.17</td>
<td>22.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.49</td>
<td>26.44</td>
</tr>
<tr>
<td>CO₂</td>
<td>190</td>
<td>1.34</td>
<td>5.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.54</td>
<td>10.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.92</td>
<td>14.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.23</td>
<td>18.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.03</td>
<td>24.85</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>0.97</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.90</td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.03</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.06</td>
<td>5.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.26</td>
<td>6.47</td>
</tr>
<tr>
<td>N₂</td>
<td>180</td>
<td>0.72</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.23</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.95</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.08</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.03</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.83</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.59</td>
<td>7.46</td>
</tr>
<tr>
<td></td>
<td>190</td>
<td>1.97</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.94</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.06</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.22</td>
<td>4.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.23</td>
<td>5.33</td>
</tr>
</tbody>
</table>