MODELING FLOW EFFECTS DURING POLYMER DECOMPOSITION USING PERCOLATION LATTICE STATISTICS

By

Daniel J. Clayton

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GRADUATE COMMITTEE APPROVAL

Of a dissertation submitted by

Daniel J. Clayton

This dissertation has been read by each member of the following graduate committee and by a majority vote has been found satisfactory.

Date	Thomas H. Fletcher, Chair
Date	William G. Pitt
Date	Kenneth L. Erickson
Date	Merrill W. Beckstead
Date	William C. Hecker

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As chair of the candidate's graduate committee, I have read the dissertation of Daniel J. Clayton in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

Date

Thomas H. Fletcher Chair, Graduate Committee

Accepted for the Department

William G. Pitt Graduate Coordinator

Accepted for the College

Douglas M. Chabries Dean, College of Engineering and Technology

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Foam encapsulants are commonly used in missile systems to increase the lifetime and reliability of the missile. The safety of the missile is greatly affected by the properties of the encapsulant. The pressure rises inside the missile as the foam degrades into smaller gaseous products, since the missile housing is essentially a closed container. If the pressure is high enough the housing may burst. The two foam encapsulants studied in this project are polyurethane foam and Removable Epoxy Foam. The ultimate goal of this project was to develop a computer model that can describe foam pyrolysis as a function of time, temperature, pressure, gas composition and confinement. The effect of pressure on foam decomposition was not well understood, with minimal of confinement effects. The effect of decomposition product flow was also not well understood. A previous model was able to empirically account for the pressure effects, but was not able to incorporate the confinement or flow effect into the foam decomposition.

Reliable pyrolysis data for both foams were obtained at atmospheric and high pressures, separate from confinement effects in this project. Buoyancy effects were found to be significant. The pyrolysis data showed that as the heating rate increased, the mass loss curves for the foam were shifted to higher reaction temperatures. A shift to higher reaction temperatures with increasing pressure and decreasing orifice size was observed. Furthermore, the decomposition product distribution shifted to produce less toluene diisocyanate and more carbon dioxide.

A model, called the MTPUF (Mass Transport PolyUrethane Model), was developed for the foam decomposition to include the capability for flow in and out of the cell. A population balance theory was the main idea that allowed for the capability of modeling the flow. Kinetic parameters were fit to the atmospheric pyrolysis data through an optimization technique. The parameters were tested against the high pressure and confinement data without being changed. The MTPUF modeling results correctly predicted the observed trend with heating rate, pressure and confinement and therefore, the MTPUF model seems capable of predicting these three effects on the polyurethane foam decomposition.

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Nomenclature

A	area under gas chromatograph peak. [mV×min]
A_i	pre-exponential factor for reaction i. [1/sec]
A_{orf}	orifice area. [cm ²]
a_i	fitted parameters for the vapor pressure of light molecules.
b_i	preexponential coefficient i.
b_n	number of distinct configurations possible for the nth-polymer fragment
	per site.
br	number of broken bridges.
C _i	charred bridge i.
C _{inert}	concentration of inert gas. [mol/cm ³]
cal	calibration factor. $\frac{mg}{L \cdot mV \cdot \min}$
C_{nmbr}	number of distinct ways to form an m-mer from a n-mer with br bridges
	broken.
$C_{\it orf}$	orifice coefficient.
d	secondary side chain.
D_i	side chain type i.
D_{AB}	diffusivity of species A into species B. [cm ² /sec]
dp	fractional change in bridges.
dsc	fractional change in side chain to bridges.
dt	timestep. [sec]
E_i	activation energy for reaction i. [cal/mol]
F	overall number of moles. [mol]
f	fraction of broken bridges.
F_n	probability that a given site is a member of the nth-polymer fragment.
fr	number of bridges formed.
<i>g</i> _{<i>i</i>}	gas species i.
h	estimated gradient distance. [cm]
K_i	"K-value" for species i.
k _i	rate constant for reaction i. [pop/sec]
L	secondary bridge.

L_i	bridge type i.
M_{c}	mass of the condensed phase. [gm]
M_{c}^{a}	adjusted mass of the condensed phase. [gm]
M_c^{in}	inflow mass of the condensed phase. [gm]
M_c^{out}	outflow mass of the condensed phase. [gm]
M_{g}	mass of the gas phase. [gm]
M_{g}^{a}	adjusted mass of the gas phase. [gm]
M_{g}^{in}	inflow mass of the gas phase. [gm]
M_{g}^{out}	outflow mass of the gas phase. [gm]
M_{i}	current mass of species i in the system. [gm]
M_i^{out}	outflow mass of the species i. [gm]
$M_{\rm inf}$	mass of infinite matrix. [gm]
M_{I_i}	mass of light molecule i. [gm]
M_n	mass of n-mer. [gm]
M_n^{brg}	mass of bridge in an n-mer. [gm]
M_{p}^{0}	original mass of polymer in the system. [gm]
M_{tot}	total mass in the system. [gm]
\dot{M}_{c}^{out}	rate of outflow mass of the condensed phase. [gm/sec]
\dot{M}_{g}^{out}	rate of outflow mass of the gas phase. [gm/sec]
\dot{M}_{i}^{gen}	rate of species i mass generation. [gm/sec]
\dot{M}^{in}_{dif}	rate of mass influx from diffusion. [gm/sec]
\dot{M}_{i}^{in}	rate of species i mass influx. [gm/sec]
\dot{M}_{i}^{out}	rate of species i mass out flow. [gm/sec]
\dot{M}_{tot}^{in}	rate of total mass influx. [gm/sec]
\dot{M}_{tot}^{out}	rate of total mass out flow. [gm/sec]
$m_{ m inf}$	mass of the infinite matrix per site. [gm/site]
m_n	mass of nth-polymer fragment per site. [gm/site]
m _{site}	mass of an extended site. [gm/site]
m_{site}^{\inf}	mass of an extended site only including the infinite matrix. [gm/site]
m0	initial mass of the sample. [gm]
Mol ^{brg}	moles of bridges in the infinite matrix. [mol]
Mol_{inf}^{exsit}	moles of extended sites in the infinite matrix. [mol]
Mol_{inf}^{sch}	moles of side chains in the infinite matrix. [mol]
$Mol_{ m inf}^{ m sit}$	moles of sites in the infinite matrix. [mol]

moles of (i+j)-mer generated. [mol]
moles of (i+j+k)-mer generated. [mol]
moles of (i+j+k+l)-mer generated. [mol]
moles of (i+j+k+l+m)-mer generated. [mol]
moles of n-mer. [mol]
moles of n-mer that broke down into a mole of an m-mer. [mol]
moles of n-mer that formed fr bridges. [mol]
moles of bridges in the infinite matrix per site. [mol/sit]
moles of bridges in the n-mer per site. [mol/sit]
moles of side chains in the n-mer per site. [mol/sit]
moles of sites in the n-mer per site. [mol/sit]
population-weighted molecular weight of the bridges. [gm/mol]
molecular weight of light molecules type i. [gm/mol]
molecular weight of species i. [gm/mol]
molecular weight of the inert gas. [gm/mol]
molecular weight of the nth-polymer fragment. [gm/mol]
population-weighted molecular weight of the side chains. [gm/mol]
population-weighted molecular weight of the sites. [gm/mol]
population of species i. [pop]
molar flux of inert gas into the cell. [mol/cm ²]
total population of species type i. [pop]
number of sites in an n-mer fragment.
maximum number of oligomer considered in the calculations.
ambient pressure. [atm]
vapor pressure of species i. [atm]
critical pressure of species i.
critical pressure of the mixture. [atm]
fraction of intact bridges.
critical fraction of bridges where the infinite matrix no longer exists.
fraction of intact bridges in only the infinite matrix.
probability of reacting with an n-mer that formed fr connections.
volumetric flow rate into the gas chromatograph. [cm ³ /sec]
nth-polymer fragment population on a per site basis.
universal gas constant. [J/mol/K]

S	total number of bridges in the nth-polymer fragment.
Т	control volume temperature. [K]
T _{ci}	critical temperature of species i. [K]
T_{cm}	critical temperature of the mixture. [K]
T_o	reference temperature. [K]
T_r	reduced temperature.
tot ^{fr}	total moles of reacted side chains. [mol]
tot_n^{fr}	total moles of reacted side chains on an n-mer. [mol]
V	number of moles in the gas phase. [mol]
V_{cell}	volume of the computational cell. [cm ³]
V_{ci}	critical molar volume of species i. [cm ³ /mol]
V_{cm}	critical molar volume of the mixture. [cm ³ /mol]
V_m	molar volume of the mixture. [cm ³ /mol]
V_r	reduced molar volume.
W _i	overall weight fraction of species i.
W_i^c	condensed phase weight fraction of species i.
W_i^g	gas phase weight fraction of species i.
W_i^{in}	inflow weight fraction of species i.
W_i^{out}	outflow weight fraction of species i.
$W_i^{(t-\Delta t)}$	overall weight fraction of species i, from the previous time step.
X _i	condensed phase mole fraction of species i.
y_i	gas phase mole fraction of species i.
Ζ	compressibility factor of the mixture.
Z_{ci}	critical compressibility factor of species i.
Z_{cm}	critical compressibility factor of the mixture.
Z_i	overall mole fraction of species i.
$Z_i^{(t-\Delta t)}$	overall mole fraction of species i, from the previous time step.

Greek Symbols

d	primary side chain.
g	ratio of specific heats.
l	primary bridge.
1	population of light molecules per bridge.
\boldsymbol{W}_i	accentric factor of species i.
\boldsymbol{W}_m	accentric factor of the mixture.
s + 1	coordination number for a Bethe lattice.
t	total number of side chains in the nth-polymer fragment.

Chapter 1. Introduction

Foam Encapsulants

Foam encapsulants are commonly used to isolate and support thermally sensitive components within missile systems. The encapsulants also assist with the mitigation of shock and vibration for the various components. The foam encapsulants increase the lifetime and reliability of the missile system. The safety of the missile is greatly affected by the properties of the encapsulant. When exposed to abnormal thermal environments, such as fire, various encapsulated safety components are designed to fail sequentially. The order in which the safety components fail depends on the degradation of the surrounding foam.

The pressure inside the container rises as the foam degrades into smaller gaseous products, since the missile housing is essentially a closed container. The container may burst if the pressure rises enough, increasing the danger, especially if the components are radioactive or explosive. The most common foams used as encapsulants are rigid, thermosetting polyurethanes and epoxies that have been thermally cured and crosslinked. Of the many encapsulants used in different systems, two rigid foams of current interest to Sandia National Laboratories are polyurethane foam (PUF) and Removable Epoxy Foam (REF).

Polyurethane Foam

Polyurethane foam is an encapsulant that has been used for many years. It is the main component in some of the older systems. Detailed information of the chemical structure of the polyurethane foam is needed to predict foam decomposition. The structural units and resulting polymeric network of many synthesized macromolecules, such as polyurethane foam, can be inferred from the starting materials and the synthesis method used to make the macromolecule. Confirmation of the structure is often obtained using infrared (IR) spectroscopy, solid-state nuclear magnetic resonance (NMR) spectroscopy, and other analytical chemistry techniques. The most common chemical structural units of the polyurethane foam and the distribution of these structural units are shown in Figure 1.1 (Hobbs et al., 1999; 2000).

These structural units were estimated from the synthesis technique (proprietary). The structural units show the polyurethane structure is a large matrix (essentially infinite) of toluene diisocyanate (TDI) groups connected by aliphatic bridges made from trimethylol propane (TMP), adipic acid (AA), diethylene glycol (DEG), and small amounts of phthalic anhydride. Mechanisms of decomposition are developed based on these structural units.

Removable Epoxy Foam

Removable Epoxy Foam is a newly developed encapsulant being considered for systems and was developed to replace Ablefoam®. Ablefoam®, a product of the Ablestick Corporation, was an epoxy foam encapsulant that contained several toxic components, including an epoxy curing agent methylene dianiline, which is a known carcinogen. Since Ablefoam® is no longer commercially available, a new foam encapsulant, Ablefoam Replacement, was developed (Rand and Russick, 1998).



Figure 1.1 Most common chemical structural units of rigid polyurethane foam. The graphic symbols represent the ingredients used to make the polyurethane foam. (Hobbs et al., 1999; 2000)

Most rigid, thermosetting epoxy foams are very difficult, if not impossible, to remove without resorting to harsh means such as chiseling or by using very aggressive solvents such as n-methyl pyrrolidinone. This has been a problem, since it is necessary at times to remove foam encapsulants to repair electrical malfunctions during system production or to rework or replace components to extend the system's lifetime. Removable foam encapsulants have long been desired for this very reason (Russick and Aubert, 2000).

Removable Epoxy Foam, which has been developed at Sandia National Laboratories, possesses properties (mechanical, thermal and electrical) similar to Ablefoam Replacement (and Ablefoam) at normal conditions, but can be dissolved in a mild solvent (e.g., n-butanol) at 90°C (McElhanon et al., 2000a). The Removable Epoxy Foam is made removable by using Diels-Alder reversible chemistry (McElhanon et al., 2000b). This foam will be used to repair and replace Ablefoam in existing systems as well as in new systems, after positive results from tests.

Major Factors

Thermal degradation of rigid polyurethane foam has been studied extensively at Sandia National Laboratories (Hobbs et al., 1999; 2000) as part of the missile safety program. Swelling of the foam and the release of gases during pyrolysis can lead to pressure rises in confined spaces, which have been observed in some confined foam decomposition experiments. However, the effect of pressure alone on foam decomposition is not well understood, in the absence of confinement effects. In this work, confinement will be referred to as physical barriers that limit the escape of decomposition products from the sample, while mass transfer will be referred to as the process in which the decomposition products leave the sample. Pressure can affect the chemical mechanism of a reaction, as well as the mass transfer, since the gas-phase diffusion coefficients are inversely proportional to pressure. The mass transfer rate, in turn, can also affect the relative rates of reversible and competing reactions. The pressure also affects the vaporization of the decomposition products. As the pressure increases, only compounds with high vapor pressures leave the condensed phase, and more decomposition products remain in the condensed phase, which encourages reversible reactions.

Knowledge of how the foam will degrade during different conditions will allow an accurate assessment of whether the safety components will fail in the correct order. This knowledge may also allow enhanced safety designs to be developed or better encapsulants could be designed in the future. For example, the components could be rearranged to allow for maximum safety, or if the foam is found to have some undesirable characteristics, the next generation foam could be modified to remove the unwanted characteristics (as in the case of Removable Epoxy Foam versus Ablefoam Replacement).

Organization of this Dissertation

Literature pertinent to the experimental techniques, along with decomposition models are presented in Chapter 2. The objectives and approach used in this study are explained in Chapter 3. The experimental apparatus used in this study are subsequently described in Chapter 4. The experimental results are then presented and discussed in Chapter 5. The modeling approach is explained in Chapter 6. Chapter 7 describes the current lattice statistics and the population balance theory developed in this study. Chapter 8 presents the techniques used to calculate the flow and phase characteristics. The techniques used to determine the various parameters used in the decomposition model are discussed in Chapter 9. Chapter 10 shows the modeling results for the various conditions. Finally, a summary of the conclusions and recommendations are made in Chapter 11.

Chapter 2. Background

This chapter is divided into five sections. Results from pyrolysis experiments conducted for the polyurethane foam and the Removable Epoxy Foam conducted at Sandia National Laboratories are shown and discussed first. Second, recent literature that discusses the use of thermogravimetry to aid in the modeling of the thermal degradation of polyurethane foams and epoxy systems are reviewed. Causes and solutions to the variation of kinetic parameters found during a literature survey will also be discussed. A description of the chemical percolation devolatilization (CPD) model (Grant et al., 1989) will then be presented next. A brief discussion of the mechanism for the atmospheric pressure degradation of polyurethane foam reported by Hobbs et al. (1999; 2000) at Sandia National Laboratories will be reviewed. Finally, mechanisms proposed for the degradation of epoxy-amine systems will also be examined.

Initial Pyrolysis Experiments

Sandia National Laboratories conducted many different pyrolysis experiments during the investigation of the decomposition of the polyurethane foam and the Removable Epoxy Foam. Initial atmospheric pressure pyrolysis experiments were conducted using a thermogravimetric analyzer at Sandia National Laboratories. Some partially-confined pyrolysis experiments were also conducted in the thermogravimetric analyzer at Sandia National Laboratories (see Ulibarri et al., 2002 for discussion of experimental technique). The gas and solid products from the thermogravimetric analyzer experiments were analyzed using a FTIR system at Sandia National Laboratories for both the polyurethane foam and the Removable Epoxy Foam (see Ulibarri et al., 2002 for discussion of experimental technique). The spectra were used to identify various chemical groups in the foams and decomposition products. These data were then used in conjunction with the elemental analysis to determine the structure of the parent and degraded foams and the decomposition products.

Some high-pressure cell, constant-load, piston displacement experiments involving larger samples (about 50-100 mg) were used to examine decomposition under highly confined conditions, to compliment the pyrolysis experiments. A few large-scale experiments were performed to obtain a good overall picture into the phenomenon occurring during pyrolysis. The foam (about 400 gm) was encased in a metal cylinder with vent holes and then heated radiantly. The results from these experiments as well as the experiments from the thermogravimetric analyzer are discussed below.

Atmospheric Pyrolysis Experiments

Atmospheric decomposition experiments were conducted for both the polyurethane foam and Removable Epoxy Foam. The experiments were conducted together with a Fourier Transform Infrared (FTIR) gas analysis system that analyzed the product gases. The mass loss curve for the atmospheric decomposition of the polyurethane foam is shown in Figure 2.1. The data were collected at a constant temperature ramp of 20° C/min in nitrogen.



As seen in Figure 2.1, there is an apparent shift in the decomposition mechanism at $\sim 350^{\circ}$ C, where the slope of the mass loss curve changes. This indicates that the decomposition has a fast low temperature step and a slower high temperature step. Gas analysis shows that the main decomposition products that were observed are toluene diisocyanate (TDI), toluene diamine (TDA), carbon dioxide (CO₂) and cyclopentanone (CPN) (Hobbs et al., 1999; 2000). The toluene diamine amounts observed were very small. Many C₅ and C₆ products were also detected. The carbon dioxide production from the decomposition increased during the second half of the decomposition.

The mass loss curve for the atmospheric decomposition of the Removable Epoxy Foam is shown in Figure 2.2. The data were collected at a constant temperature ramp of 20° C/min.



The mass loss curve for the Removable Epoxy Foam is very different than the mass loss curve for the polyurethane foam, as there appear to be multiple steps, as seen in Figure 2.2. At 150°C the mass loss curve drops dramatically to ~85% of the initial sample mass, and then slowly decreases. At 230 and 340°C the slope of the mass loss curve increases. At 500°C the slope decreases, until at 600°C the sample is only ~5% of the initial sample mass. The preliminary gas analysis shows that the main decomposition products are phenol-based molecules, along with some siloxanes. The initial chemical structure of the Removable Epoxy Foam had not been worked out in detail before this project.
Partially-Confined Pyrolysis Experiments

Some partially-confined atmospheric pyrolysis experiments were conducted at Sandia National Laboratories (see Ulibarri et al., 2002 for discussion of technique). These experiments were designed to measure the confinement effects. As discussed earlier, the confinement refers to physical barriers that restrict the removal of the decomposition products. Varying degrees of confinement were achieved by using hermetically sealed aluminum pans with lids that contained small orifices. Greater degrees of confinement were obtained with smaller orifices. A pictorial representation of how the confinement was varied is shown below in Figure 2.3.



Figure 2.3 Graphic of how the confinement was varied.

As seen in Figure 2.3, the flow in and out of the basket becomes more restricted as the orifice size decreases. If the rate of gas generation during the decomposition process is high enough, the flow through the orifice may even choke, causing the pressure inside the pan to rise. These partially-confined experiments were conducted in a thermogravimetric analyzer (TGA) at Sandia National Laboratories with a heating ramp of 20° C/min. The experiments were duplicated to ensure the accuracy of the data. The

pans were \sim 4 mm in diameter and \sim 2.6 mm tall. The orifice sizes ranged from 2.0 to 0.06 mm. The sample sizes inside the baskets ranged from 1.5 to 2.0 mg. Plots of the partially-confined data for both the polyurethane foam and the Removable Epoxy Foam are shown below in Figures 2.4 and 2.5.



Figure 2.4 Comparison of the partially-confined experiments for the polyurethane foam. (20°C/min) (Ulibarri et al., 2002)

As seen in Figure 2.4, for the polyurethane foam, as the orifice size decreased, the mass loss curve shifted to the higher temperatures. The 2 mm orifice data is on average 20° C higher than the unconfined data. As the orifice size decreases from 2 to 1 mm, the shift increases to 30° C. When the orifice size is decreased to 0.4 mm, the shift increases to 50° C. The 0.2 mm data are shifted about 60° C from the unconfined data. As the orifice size decreases to 0.06 mm, the mass loss curve is shifted 70° C from the

unconfined data. Furthermore, the change in the decomposition mechanism at $\sim 350^{\circ}$ C seen in the unconfined experiments, appears to disappear in the partially-confined experiments.



As seen in Figure 2.5, the mass loss curve also shifted to higher temperatures as the orifice size decreased for the Removable Epoxy Foam. The 2 mm orifice data are on average 40°C higher than the unconfined data. The shift increased to 45°C as the orifice size was decreased from 2 to 1 mm. The shift increases to 50°C, when the orifice size decreased to 0.4 mm. The 0.2 mm data are also about 50°C higher than the unconfined data. As the orifice size decreases to 0.06 mm, the mass loss curve is also shifted about 50°C from the unconfined data.

The production of carbon dioxide increased as the orifice size decreased during the polyurethane foam partially-confined experiments. Furthermore, the increase in carbon dioxide production appears to correspond with a decrease in the toluene diisocyanate production. This change in the decomposition products suggests that the confinement affects the different decomposition pathways during the pyrolysis. The gas analysis of the Removable Epoxy Foam decomposition products currently showed no change in the distribution of the decomposition products with decreasing orifice size.

Totally-Confined Pyrolysis Experiments

Some totally-confined experiments were also conducted at Sandia National Laboratories to complement the partially-confined and atmospheric pressure experiments (see Ulibarri et al., 2002 for discussion of technique). High-pressure cell, constant-load, piston displacement experiments involving larger samples (about 50-100 mg) were used to examine decomposition under highly confined conditions, in which mass transfer is highly limited and the effects of any reversible or secondary reactions would be most significant. The experimental arrangement for examining the response of polyurethane foam to heating under confinement is shown in Figure 2.6. The piston displacement was measured while the foam decomposed. The load on the foam sample was varied while the experiments were heated to a temperature of about 300°C and then held at that temperature for one or two hours. Data from two of the piston experiments showing the displacement versus time are presented in Figure 2.7.



Figure 2.6 Schematic of the totally-confined experiment apparatus. (Ulibarri et al., 2002)



Figure 2.7 Piston displacement versus time for two different average pressures (P_{ave}) during the experiments. Data from Erickson (2002)

As seen in Figure 2.7, the displacement starts to increase at around 60 minutes, and then slowly increases as the experiment continues. This indicates that the increase in the displacement may be caused by the breakdown of the foam into smaller components, which exhibit higher vapor pressures. Furthermore, at approximately 50 minutes, the temperature of the reactor has reached the ~300°C temperature setting, and so the increase in the displacement could not be from an increase in the reactor temperature. The partially-confined and the totally-confined experiments were designed to measure the confinement effects on the foam decomposition. The previous decomposition model for the polyurethane foam was not able to incorporate the confinement effects.

Large-Scale Pyrolysis Experiments

During the above pyrolysis experiments, evidence of a "flowing" condensed phase was observed with both the polyurethane foam and the Removable Epoxy Foam. The effect of the flow of this condensed phase on the decomposition of the foam needed to be known. Some large-scale experiments were conducted, where the foam (about 400 gm) was encased in a metal cylinder with vent holes and then heated radiantly. Samples were heated from the top, or the bottom, or the side to further explore the flow effects occurring in each heating orientation. The samples were photographed using x-ray equipment at Sandia National Laboratories, as a function of time. An example picture of a top-heated experiment is shown in Figure 2.8. This picture was taken after the sample was heated from the top for 30 minutes. The light gray lines in Figure 2.8 are the thermocouples that were placed in the foam for the experiment. The thick dark gray line in the middle of Figure 2.8 is the reaction front with the condensed phase resting on top of the remaining foam sample. As the experiment progressed, the reaction front moved down the canister.



Figure 2.8 Example x-ray photograph of a large scale pyrolysis experiment.

It was found that for the bottom-heated experiment, the decomposition of the foam was approximately twice as fast as the top-heated experiment. The reaction front became curved as the decomposition products ran toward the sides and then left the container before vaporizing during the bottom-heated experiment. The decomposition time for the side-heated experiment was between the top- and bottom-heated experiments. The increase in the rate of decomposition was attributed to the fact that the condensed decomposition products flowed out of the cylinder as the foam was decomposing. For the side- and bottom-heated experiments, the condensed phase decomposition products were flowing out of the cylinder. The heat that would have been used to vaporize the decomposition products was now applied directly to the foam, causing a higher rate of decomposition. These large-scale experiments, along with the thermogravimetric pyrolysis experiments, help provide a good basis for the analysis of the foam decomposition.

Thermogravimetry

One way to determine how the foam will degrade with different thermal conditions is thermogravimetry. Thermogravimetry involves the measurement of the sample weight while heat is applied. Usually the weight and temperature of the sample are recorded over a certain time period and then analyzed. One advantage to thermogravimetry is that the heating rate can be controlled and varied quite easily. Constant temperature periods can also be used in sequence with heating ramps. The composition of the gases flowing past the sample can be easily regulated and collected. A near continuous weight measurement allows for a dynamic as well as ultimate analysis. Some experiments allow for pressure regulation as well. With a continuous flow and small sample size, the degradation products are quickly removed so the effects of pressure can be considered with minimal confinement and mass transfer effects.

There are a few difficulties with thermogravimetric analysis. Thermogravimetry alone gives no information on the chemical nature of the degradation products. Another challenge is that with some systems, buoyancy effects are very pronounced and can influence the data. Also, the temperature measurement can be inaccurate if not properly calibrated. Normally the sample temperature is determined by measuring the gas temperature near the sample. There could be a large temperature difference or delay between the sample temperature and the surrounding gas temperature, if the heat transfer is slow, and this may significantly affect the results.

Use of Thermogravimetry in Thermal Degradation

To accurately model the thermal degradation of any foam, a mechanism must be proposed, and the respective kinetic parameters must be determined. Thermogravimetric analysis is a useful tool for obtaining kinetic parameters, once the chemical mechanism is understood. Usually, the mechanism is proposed through evidence found in the differences between the chemical structures of the parent and degraded foams, and through analysis of the evolved gaseous products. Once a mechanism is proposed, thermogravimetric analysis is frequently used to study the overall thermal degradation kinetics of polymers, because it gives reliable information on the frequency factor, the activation energy and the overall reaction order (Park et al., 2000).

There are examples in the literature that use thermogravimetry to obtain kinetic parameters for polyurethane foams. In one case, Hobbs et al. (1999; 2000) used thermogravimetric data to evaluate kinetic parameters for the degradation of rigid polyurethane foam at atmospheric pressure. Ramakrishnan (1975) used thermogravimetric data to fit an empirical power-law model that described the effect of the thermal stability from adding fire-retardant substances to polyurethane foams. Examples in the literature that illustrate the use of thermogravimetry during the study of various epoxy systems are discussed below. Buch and Shanahan (2000a; 2000b) used gravimetric data to determine the behavior of the thermal degradation of a structural epoxy adhesive. Xiao and Shanahan (1997) employed thermogravimetric analysis to determine the water absorption and desorption in an epoxy resin. Su et al. (2000) used thermogravimetry to study the effects of chemical structure changes on thermal, mechanical, and crystalline properties of rigid rod epoxy resins. Finally, Dyakonov et al. (1996) used thermogravimetry to study the thermal degradation of some aromatic amine-cured model epoxy resin systems.

Variation in Literature Parameters

Discrepancies often occur between published kinetic parameters determined by thermogravimetry for the degradation of various polymers. For example, many different activation energies are reported in the literature even for a simple polymer such as polyethylene. Reported activation energies for high-density polyethylene (HDPE) and low-density polyethylene (LDPE), as researched by Park et al. (2000), are shown in Table 2.1. The reported activation energies vary by ~120 and ~150 kJ/mol, for HDPE and LDPE, respectively. This variation in activation energies is not desirable when used to design highly sensitive equipment.

Many researchers believe that carelessness is the cause for the disagreement in the rate parameters shown in Table 2.1. Park et al. (2000) suggest that the variations in the calculated kinetic parameters depend upon the mathematical approach taken in the analysis. Grønli et al. (1999) looked at the different configurations of the experimental

equipment for an explanation of the variance. The recommendations of Park, Grønli, and

their respective coworkers, are discussed below.

Pafaranaas	Activation Energies (kJ/mol)					
References	HDPE	LDPE				
(Mucha, 1976)	247-330 ^{a,b}	163-230 ^{a,b}				
(Urzendowski and	304 ^c	290 ^c				
Guenther, 1971)	320 ^b	303 ^b				
(Wu et al., 1993)	234 ^b	206 ^b				
(Westerbout et al. 1997)	220 ^b	241 ^{b,d}				
(Westernout et al., 1997)	-	201 ^{b,d}				
(Jellinek, 1950)	-	192-276 ^a				
(Park et al., 2000)	338 ^e	196 ^e				

Table 2.1	Comparison of Reported Activation Energies for HDPE and LDPE
	[adapted from Park et al. (2000)]

^a Activation energy decreases with increasing molecular weight of sample.

^b Measurements performed in a nitrogen environment.

^c Measurements performed in a vacuum environment.

^d Different initial molecular weight distributions.

^e Different heating rates.

There are many different ways to analyze kinetic data. Park et al. (2000) state that discrepancies indicate problems in the selection and utilization of different analytical methods to describe the thermal degradation of polymers. For example, the Flynn-Wall method (Park et al., 2000) uses only one point, i.e. the point of maximum rate, and is therefore, regarded more of a scoping experiment than an experiment for detailed kinetic evaluation. Wide deviations were found between reported activation energies using methods with single heating rate experiments. It was observed that the best methods for analyzing data utilized data collected at a range of heating rates. Park and coworkers concluded that a dynamic method, which uses multiple heating rates, would give the best results. Hobbs et al. (1999; 2000) used a dynamic least-squares method with optimization software to determine the kinetic parameters. They then tested the parameters on different heating rate experiments as an assessment of the parameters. This technique seemed to give superior results and fit a large range of data.

Thermogravimetric Analyzer Configuration

Several styles of thermogravimetric analyzer configurations are commonly used. Grønli et al. (1999) studied eight different thermogravimetric analyzers: three were TA Instruments model SDT 2960, two were Perkin-Elmer model TGA 7, one was a Perkin-Elmer model TGS 2, one was a Mettler Toledo model TGA/SDTA 851^e, and one was a Netzsch STA 409C instrument. Figure 2.9 displays schematics of these five different thermogravimetric analyzers with their respective flow paths, sample holders and microbalance arrangements. As seen in Figure 2.9, the TA Instruments model SDT 2960 and the Mettler Toledo model TGA/SDTA 851^e have flow over the top of the sample, while the Perkin-Elmer model TGA 7, Perkin-Elmer model TGS 2, and the Netzsch STA 409C have flow around the sample.

Grønli et al. (1999) affirm, "In our experience, the scatter in experimental data displayed in this paper well represents the current state of the art. Careful work reported by esteemed colleagues in the prior literature no doubt incurred similar (if not worse) instrumental errors . . . Significant uncertainties are present in data obtained from the best state-of-the-art instruments. Unfortunately, we are not aware of any other experimental techniques which offer more reliable data . . . we recommend that all researchers heed the impact of systematic errors on their interpretation of thermobalance data." The

thermogravimetric analyzer used in this research is of the same configuration as the Perkin-Elmer model TGA 7 and the Perkin-Elmer model TGS 2, and will be described in greater detail in a later section.





Figure 2.9 Schematic of thermogravimetric analyzers used in study (Grønli et al., 1999).

Grønli et al. (1999) obtained good agreement between all of the different configurations, except for two data sets. In their paper, Grønli and coworkers did not specify which instrument corresponded to which number. The data sets at the 5°C/min condition for analyzers #1 and #5 were significantly different than the other six curves (analyzers #2-4 and 6-8). At the 40°C/min condition, all the data sets were within the experimental scatter. The 5°C/min condition was used as the comparison, because with the slower heating rate, the inherent differences between the various configurations would be minimized.

The activation energy for the cellulose pyrolysis for the six accepted data sets (analyzers #2-4 and 6-8) at the 5°C/min condition ranged from 236-257 kJ/mol, and the

activation energy ranged from 211-232 kJ/mol for the eight data sets at the 40°C/min condition. This difference in activation energies at different heating rates was attributed to an increase in thermal delay between the measured temperature and the actual temperature. As the sample size was decreased from five to one mg, the activation energy at the 40°C/min condition approached the value at the 5°C/min condition. Since the shapes of the curves were all similar, the only difference being a translation in time/temperature, Grønli et al. (1999) concluded that the differences were attributed to the thermal delay for the different configurations.

Grønli et al. (1999) constructed a graph to display the weight loss sensitivity to the kinetic parameters determined by thermogravimetry as a display of the error produced by the different configurations. To prove their point, they used the largest, smallest, and mean values for the kinetic parameters calculated from the six accepted data sets at the 5° C/min condition to calculate the weight loss and its derivative as a function of temperature. (see Figure 2.10) The m/m_o curve starts at 1.0 and decreases to ~0.05 (left axis), while the –dm/dt curve starts and ends at 0.0 (right axis). As seen in Figure 2.10, the overall weight loss curve and its derivative are very similar with the different kinetic parameters.

The conclusion of the review of thermogravimetry is that meaningful thermogravimetric analyzer data can be obtained with any configuration, as long as the thermal delay is minimized. Care was taken to ensure that the thermal delay for the configuration used in this project was minimized by using helium as the inert atmosphere, and decreasing the basket size. This is explained in more detail in Chapter 5. Furthermore, a dynamic data analysis method, which uses multiple heating rates, was shown to give the best results. A similar method to that used by Hobbs et al. (1999; 2000) was used to determine the kinetic parameters for the pressure dependent degradation of the polyurethane foam and is discussed in Chapter 8.



Figure 2.10 Sensitivity of weight loss to kinetic parameters, showing the largest (- -), smallest (--), and mean values (O) (Grønli et al., 1999).

Chemical Percolation Devolatilization Model

The chemical percolation devolatilization (CPD) model (Grant et al., 1989) was originally developed to model coal devolatilization. The discussion of the CPD model presented here is adapted from the documentation of Grant et al. (1989) and Fletcher et al. (1992a; 1992b). Coal is visualized as an infinite array of fused aromatic rings, of various sizes and types (clusters) in this model. These clusters are connected with a variety of chemical bridges, some containing labile bonds that will break readily during pyrolysis, and other bridges that remain stable throughout a given process. Fragments are formed when the labile bonds break. More and smaller fragments are generated as more bridges break. A fragment may change phase and then be transported away from the infinite array, depending on the conditions. These gaseous fragments constitute the devolatilization products.

The CPD model includes a chemical mechanism that establishes the bond breaking and product formation sequences. The CPD model uses the desirable features of percolation theory for determination of the degree of lattice separation. Bethe pseudolattice statistics, with closed-form mathematical solutions, are used to predict the distribution of the gaseous product sizes as well as the fraction of material in the remaining infinite array (char). Finally, vapor-liquid equilibrium is used to determine which fragments change phase and are transported away from the infinite array. These three processes are discussed in further detail below.

Chemical Mechanism

The simple reaction sequence proposed in the CPD model starts with the activation of a chemical bond in a labile bridge to form a highly reactive bridge intermediate that is rapidly consumed by one of two competing processes. The reactive bridge material may either be released as a gaseous product, with the concurrent relinking of the two associated sites; or else side chains are produced from the reactive bridge fragments. These stabilized side chains may be converted eventually into light gas fragments through a subsequent, slower reaction. Thus, the following scheme is proposed to represent the devolatilization process:

i. formation of a reactive bridge intermediate from a labile bridge

$$\ell \xrightarrow{k_b} \ell^* \tag{2.1}$$

ii. formation of a char bridge and gas from the reactive intermediate

$$\ell^* \xrightarrow{k_c} c + 2g_2 \tag{2.2}$$

iii. formation of a side-chain from the reactive intermediate

$$\ell^* \xrightarrow{k_d} 2d \tag{2.3}$$

iv. conversion of side chains into light gases

$$d \xrightarrow{k_s} g_1 \tag{2.4}$$

The reactive bridge intermediate, ℓ^* , is formed from labile bridges, ℓ , by a relatively slow step with rate constant k_b followed by the two rapid competitive processes with rates k_d and k_c to produce side chains, **d**, and stable charred bridges, *c*, respectively. The differential equations governing bridges and reactive intermediates are:

$$d\ell/dt = -k_b\ell \tag{2.5}$$

$$d\ell */dt = k_b \ell - (k_d + k_c)\ell *$$

$$(2.6)$$

where the symbols for the various species also represent their fractional abundance expressed as normalized bridge parameters. With a steady-state approximation for ℓ^* $(d\ell^*/dt \cong 0)$, an algebraic estimate of ℓ^* is made:

$$\ell^* \cong k_b \ell / (k_d + k_c) = k_b \ell / k_c (\mathbf{r} + 1)$$
(2.7)

where $\mathbf{r} = k_d / k_c$. This expression for ℓ^* can be used to calculate the other variables in the reaction scheme as follows:

$$dc/dt = k_c \ell^* \cong k_b \ell/(\mathbf{r}+1)$$
(2.8)

and likewise

$$d\mathbf{d}/dt = 2k_{d}\ell^{*} - k_{g}\mathbf{d} \cong 2\mathbf{r}k_{b}\ell/(\mathbf{r}+1) - k_{g}\mathbf{d}$$
(2.9)

$$dg_1/dt = k_g \mathbf{d} \tag{2.10}$$

$$dg_2/dt = 2\,dc/dt\tag{2.11}$$

The fraction of intact bridges, p, may be calculated from the labile (ℓ) and char (c) bridges as follows:

$$p = \ell + c \tag{2.12}$$

The bridge populations are normalized by the number of bridges in a totally connected lattice The fraction of broken bridges, f, is therefore:

$$f = 1 - p \tag{2.13}$$

Percolation theory places no limit on the kinds of bridges that may be used to characterize the system providing they can be partitioned into either intact or broken bridges.

Percolation Lattice Statistics

In an infinite array with many labile bonds available to be broken, the number of fragments generated is nonlinear compared to the number of bonds broken. For example, in an infinite array with each cluster connected by bridges to four neighboring clusters, no detached clusters result when only two or three bridges are broken. This effect is illustrated clearly by Grant, et al. (1989) using a Monte Carlo simulation. Monte Carlo simulations of bridge breaking are suitable for describing lattice features, but they are computationally demanding. Percolation theory provides a more computationally efficient way to simulate pyrolysis reactions. Loops in real lattices, which link two or more sites through more than one pathway, prevent simple analytical expressions for the

essential statistical quantities characterizing these lattices. The use of Bethe pseudolattices or trees resolves this difficulty by removing the possibility of looping. The pseudo-lattices have many properties similar to real lattices for those problems in which only the smaller finite clusters and the infinite arrays are important. The statistical results from using Bethe pseudo-lattices have been shown to produce minimal error from simulations with loop structures. These conditions apply very well to the devolatilization of coal, as well as foam decomposition with minimal error.

The expressions for statistical quantities used in the CPD model are given based on site counting, but the conversion between these expressions and the corresponding statistical expressions based on bridge counting are straightforward and depend on the coordination number. The coordination number is the total number of attachments per cluster. The coordination number of a Bethe pseudo lattice is denoted by "s + 1" For mathematical convenience. Lattice evolution is characterized by a time-dependent fraction (p) of bridges that remain intact, the remaining fraction, (1-p), having been broken. If bridge scission events are statistically independent, the probability (F_n) that a given site is a member of a cluster of n sites with s bridges becomes:

$$F_{n}(p) = nb_{n}p^{s}(1-p)^{t}$$
(2.14)

where the values of s and t are given by:

$$s = n-1$$
 $t = n(s-1)+2$ (2.15)

The variable t is the number of broken bridges on the perimeter of a s-bridge cluster. The severed bridges serve to isolate the cluster from all other sites or clusters. The quantity nb_n given in Equation 2.14 is the number of distinct configurations possible for a cluster of size n containing a given site, and b_n is the same quantity expressed on a per site basis. The equation for nb_n is:

$$nb_{b} = \frac{\boldsymbol{s}+1}{\boldsymbol{s}+\boldsymbol{t}} \binom{\boldsymbol{s}+\boldsymbol{t}}{\boldsymbol{s}} = \frac{\boldsymbol{s}+1}{n\boldsymbol{s}+1} \binom{n\boldsymbol{s}+1}{n-1}$$
(2.16)

with the binomial coefficient given for non-integer indices \mathbf{m} and \mathbf{h} , given by:

$$\binom{\boldsymbol{m}}{\boldsymbol{h}} = \frac{\Gamma(\boldsymbol{h}+1)}{\Gamma(\boldsymbol{m}+1) \cdot \Gamma(\boldsymbol{h}-\boldsymbol{m}+1)}$$
(2.17)

where Γ is the standard gamma function. Here, non-integers arise from fractional values for s + 1, which might be interpreted as average values for lattices with mixed coordination numbers. The use of Equations 2.14, 2.16 and 2.17 gives an analytical expression for the probability of finding a cluster of size n with a bridge population p.

The total fraction of sites, F(p), contained in all of the finite clusters is:

$$F(p) = \sum_{n=1}^{\infty} F_n(p) = \left[\frac{1-p}{1-p^*}\right]^{s+1} = \left[\frac{p^*}{p}\right]^{(s+1)/(s-1)}$$
(2.18)

where p^* is the root of the following equation in p:

$$p^* (1 - p^*)^{s-1} = p(1 - p)^{s-1}$$
(2.19)

The value of $p^*(1-p^*)^{s-1}$ passes through a maximum at p=1/s, the so-called percolation threshold or critical point. This is the point where statistically the lattice is no longer an infinite array with finite pieces, but only finite pieces. Below the critical point the appropriate solution of Equation 2.19 is the trivial one of $p^* = p$. For p > 1/s the nontrivial solution of Equation 2.19 may be used to evaluate the p^* needed in

Equation 2.18 to calculate F(p). Conveniently, the appropriate root for p^* always falls in the range $0 < p^* < 1/s$ for values of p both above and below the critical point, and these values are readily obtained from Equation 2.19 using simple numerical methods. A plot of F(p) versus p is given below in Figure 2.11 for several different values of s + 1to illustrate the nonlinear dependence of F(p) upon p. The point at which F(p) drops sharply from unity is the so-called percolation threshold or critical point (p_{crit}).



Figure 2.11 Values of F(p), fraction of total sites contained in finite fragments, versus p, fraction of intact bridges, for various coordination numbers.

Vapor-Liquid Equilibrium

The fraction of the fragments that change phase can be determined by using a simple vapor-liquid equilibrium relationship using Raoult's law. A standard multi-component isothermal flash calculation is used with the Rachford-Rice equation (Seader

and Henley, 1998) to determine the split between vapor and liquid by solving the following equation for V/F:

$$0 = \sum_{i=1}^{n} \frac{z_i (K_i - 1)}{(K_i - 1)\frac{V}{F} + 1}$$
(2.20)

where

$$K_i = \frac{y_i}{x_i} = \frac{P^*}{P} \tag{2.21}$$

V/F is determined iteratively. The parameters z_i , x_i , and y_i represent mole fractions in the feed, liquid phase, and vapor phase, respectively. V and F represent the total moles in the vapor phase and in the feed, respectively. P^* represents the vapor pressure of the pure component at the system pressure, P. The mole fractions in the liquid and vapor phases can be determined as follows:

$$x_{i} = \frac{z_{i}}{(K_{i} - 1)\frac{V}{F} + 1}$$
(2.22)

and

$$y_{i} = \frac{K_{i}z_{i}}{(K_{i} - 1)\frac{V}{F} + 1}$$
(2.23)

The "K-values" defined in Equation 2.21 can be determined from the vapor pressure of the pure components, P^* , divided by the system pressure, P. A vapor pressure correlation for coal tars known as the Fletcher-Grant-Pugmire (FGP) correlation (Fletcher et al., 1992a; 1992b), compares well with boiling point data for 111 organic compounds at pressures of 0.007, 0.08, 1, and 10-atm, and has the following form:

$$P_n^* = 87100 \cdot \exp\left(\frac{-299 \cdot M_n^{0.5903}}{T}\right)$$
(2.24)

where P_n^* is the vapor pressure of the pure nth-polymer fragment in atmospheres, M_n is the molecular weight of the nth-polymer fragment in gm/mol, and T is the temperature in K. The functional form of Equation 2.24 is similar to the Clausius-Clapeyron equation.

The percolation lattice statistics in combination with the vapor liquid equilibrium characterized the release of gaseous products in coal devolatilization experiments very well. The computational technique is much more efficient than Monte Carlo methods. The nonlinear nature of percolation statistics produces an appropriate representation of the functional form of gaseous product release. The CPD model also provides the molecular weight distribution of the gaseous and condensed products.

Mechanism for Polyurethane Foam Degradation

The polyurethane foam decomposition model developed by Hobbs et al. (1999; 2000) is an extension of the CPD model (Grant et al., 1989) and is the first attempt to describe degradation of a polyurethane foam using percolation theory with vapor-liquid equilibrium. Similarly to the CPD model, percolation lattice statistics using Bethe lattices is used to characterize the degraded foam structure with regard to the size and concentration of finite fragments. A standard multi-component isothermal flash calculation was used to determine the split between vapor and condensed phases following the same procedure used by Fletcher et al. (1992a; 1992b).

The major difference between the CPD model and the polyurethane foam degradation model is the kinetic scheme. The rate equations for the kinetic scheme for

the polyurethane foam are shown below in Table 2.2. A schematic drawing of the kinetic scheme is shown in Figure 2.12.

Species	Rate Equation		
ℓ	$d\ell/dt = -k_1\ell - k_2\ell + k_3\boldsymbol{d}$		
L	$dL/dt = k_5 d^2 - k_6 L - k_7 L + k_8 d$		
d	$d\boldsymbol{d}/dt = k_2\ell - k_3\boldsymbol{d} - k_4\boldsymbol{d} - 2k_5\boldsymbol{d}^2$		
d	$dd/dt = k_7 L - k_8 d - k_9 d$		
c_1	$dc_1/dt = k_1\ell$		
c_2	$dc_2/dt = k_6 L$		
g_1	$dg_1/dt = k_1\ell$		
g_2	$dg_2/dt = k_4 d$		
g_3	$dg_3/dt = k_5 d^2$		
84	$dg_4/dt = k_6 L$		
g_5	$dg_5/dt = k_9 d$		

Fable 2.2	Rate equations for the atmospheric pressure rigid polyurethane foam
	degradation model (Hobbs et al., 1999; 2000).



Figure 2.12 Polyurethane foam bridge breaking mechanism (Hobbs et al., 1999; 2000).

This 9-step mechanism with 11 "species" is described below.

- 1. Evolution of a light gas product without chain scission of the primary polymer.
- 2. Chain scission of the primary polymer.
- 3. Chain recombination of the primary polymer fragments.

- 4. Evolution of a light gas product from the product of Step 2.
- 5. Reaction of product from Step 2 to form a secondary polymer.
- 6. Evolution of a light gas product without chain scission of the secondary polymer
- 7. Chain scission of the secondary polymer.
- 8. Chain recombination of the secondary polymer fragments.
- 9. Evolution of a light gas product from the product of Step 7.

The symbols ℓ (or *L* as seen in Figure 2.12), and L represent thermally unstable bridges in the primary and secondary polymers. Thermally stable bridges in the primary and secondary polymer are represented by c_1 and c_2 . The thermally stable bridges are actual bonds and do not contain mass in this mechanism. Decomposing polyurethane foam produces a char, or carbonaceous residue, that is thermally stable under certain conditions. The formation of thermally stable bonds contributes to char formation. The symbols *d* and d represent side-chains in the primary and secondary polymers, respectively. Various gaseous products are represented by g, g, g₃, g₄, and g. This primary/secondary polymer system was developed through evidence observed in the thermogravimetric analysis of the foam at atmospheric pressure (Hobbs et al., 1999; 2000) and appears to fit the data.

The dynamic variables of the percolation theory, which are slightly different from the CPD model, are the bridge population parameters, ℓ , L, c₁ and c₂, from which the number of intact bridges, p, may be calculated:

$$p = \ell + L + c_1 + c_2 \tag{2.25}$$

The other variables, including the vapor-liquid equilibrium, are still treated in the same manner as discussed in the CPD model.

Mechanisms for Amine-Cured Epoxy Degradation

The structure of the Removable Epoxy Foam is predominantly formed from the reaction of diglycidyl ether of bisphenol A (DGEBA), with a mixture of amine-containing components. Consequently, a literature search was conducted on mechanisms with amine-cured epoxy resin systems. The only literature example for the degradation of amine-cured epoxy resin systems was written by Dyakonov et al. (1996). In this paper, the degradation of seven different amine-curing agents mixed with DGEBA is briefly described. A single-step degradation process was observed for all seven cases. They classified the degradation process as a chain scission, and gave respective activation energies for each different compound. They were not specific as to which parts of the chain were broken. The activation energies were calculated by the Flynn-Wall and Kissinger (Park et al., 2000) methods with good agreement, and ranged from 160-200 kJ/mol. They did not detect any change in the mechanism throughout their experiments from 20 to 800°C. The majority of the compounds had ~20% of the original sample remaining as a thermally stable residue.

Based on atmospheric pressure thermogravimetric data for Removable Epoxy Foam, a single chain scission step does not appear adequate. Preliminary experiments with the Removable Epoxy Foam indicate the formation of a "liquid" or flowing phase during decomposition, and that only ~5% of the original foam does not pyrolyze. The effects of the "liquid or flowing phase, along with the multiple chain scission steps will be required in an accurate decomposition model. Furthermore, the structure of the Removable Epoxy Foam was not well known before this project.

Chapter 3. Objectives

The ultimate goal of this project is to develop a computer model that can describe foam pyrolysis as a function of time, temperature, pressure, gas composition and confinement. The effect of pressure alone on foam decomposition is not well understood, in the absence of confinement effects. The effect of decomposition product flow is also not well understood. A model was developed prior to this study (Hobbs et al., 1999; 2000) based on the CPD approach (Grant et al., 1989) for the polyurethane foam. No such model exists for the Removable Epoxy Foam. The previous model was able to empirically account for pressure effects, but was not able to incorporate confinement and flow effects into the foam decomposition.

The first objective of this research was to obtain reliable pyrolysis data for both the rigid polyurethane foam and the Removable Epoxy Foam at both atmospheric and high pressures, with as few confinement effects as possible. The data from the first objective were used to support development of a kinetic scheme for the polyurethane foam decomposition, (second objective,) in collaboration with Sandia National Laboratories. The third objective was to develop a new model that extends the CPD approach to include mass transfer and confinement effects. This new model, called MTPUF (Mass Transfer PolyUrethane Foam) model, was then tested incorporating the polyurethane foam decomposition mechanism. The first and third objectives were accomplished specifically in this research, while the second objective was a collaborative effort with Sandia National Laboratories.

Initial plans on this project called for the MTPUF model to be modified for use with the Removable Epoxy Foam. The initial task was therefore to determine the chemical structure of the Removable Epoxy Foam. This initial task was accomplished and is explained in detail in Appendix A. However, the Removable Epoxy Foam was not modeled in this project. One reason for not modeling the Removable Epoxy Foam is the complication of the foam solubility. The foam was designed to break down when heated in the presence of solvents. As the initial break down of the polymer forms small solvent molecules, the new solvent molecules can dissolve the foam, which then can allow the foam to transported out of the computational cell. The solubility of the foam in the various solvents needs further exploration before comprehensive modeling can take place. Furthermore, the Removable Epoxy Foam is undergoing reformulation to change various properties (i.e., glass transition temperature, etc.) The basic structure of the foam is currently being changed occasionally, while other properties needed in the modeling (i.e., density, thermal conductivity, etc.) may change with the reformulation. Until a specific formulation is selected, the modeling of the decomposition must be postponed. The pyrolysis data, as well as the determination of the initial structure of the Removable Epoxy Foam, were obtained using the first chemical formulation. For these reasons, the modeling of the Removable Epoxy Foam was not performed as part of this dissertation.

Chapter 4. Experimental Apparatus

Various types of equipment were used to obtain data to determine the decomposition mechanism for the polyurethane foam and the Removable Epoxy Foam. Atmospheric and high pressure pyrolysis experiments were performed in a high pressure thermogravimetric analyzer. Gaseous pyrolysis products from atmospheric and high pressure pyrolysis experiments were analyzed through the use of a gas chromatograph and a FTIR system. Parent and degraded foam compositions were determined through elemental analysis. Each of these systems will be discussed in more detail in this chapter.

High Pressure Thermogravimetric Analyzer

The Deutsche Montan Technologie (DMT) high pressure thermogravimetric analyzer (HPTGA) (Figure 4.1) is an electrically-heated apparatus that allows the control of temperature, pressure, gas concentrations, and flowrates. A sample is suspended from a chain attached to the microbalance. The sample is lowered into the furnace. The weight of the sample is then measured and recorded throughout the experiment. The temperature is monitored with thermocouples. The maximum reactor temperature is 1100° C. The maximum heating rate achievable in the reactor is 100° C/min. The pressure is controlled through a pressure control valve, with an accuracy of $\pm 1\%$. The entire vessel is rated at a maximum pressure of 100 bar. The gas concentrations and flowrates are regulated with mass flow controllers. The flowrates can range from 0.1 to 10 L/min. Some of the gases that have been used in the HPTGA include helium, nitrogen, oxygen, carbon dioxide, carbon monoxide, argon, hydrogen, and methane. The composition of the gas can be changed by the relative flowrates.



Figure 4.1 Schematic of the DMT high pressure thermogravimetric analyzer.

A computer uses TGAsoft[®] software from DMT to record the time, temperature, pressure, and weight of the sample during a cycle. The gas temperature is measured with the sample temperature probe. The sample temperature is assumed to be equal to the measured temperature. Helium was chosen as the inert gas environment due to its high thermal conductivity and low density, which should minimize the thermal delay and buoyancy effects, and hence increase the accuracy of the data. A more detailed discussion of the buoyancy effects is presented in a later section.

Sample Holders

The samples were held in baskets as they were heated in the HPTGA. Two different styles of baskets were designed during this project, as shown in Figure 4.2. The first style of basket was constructed from a very fine Incoloy mesh. The mesh allows for intimate contact between the sample and the inert atmosphere, increasing the removal of the gaseous products as well as increasing the heat transfer between the sample and the inert atmosphere. The conical mesh style basket (Figure 4.2a) weighed about 0.1 gm., with an average diameter of 0.28 in. and a height of 0.48 in.

The second style of basket (Figure 4.2b) was constructed from solid Incoloy metal. Incoloy metal was chosen as the material of construction, to ensure the same thermal and reaction behavior of the basket as with the Incoloy mesh. The first solid basket weighed ~1.5 gm. (0.5 inch diameter), and did not allow for consistent data. It was assumed that the basket was big enough to occasionally touch the side of the reactor, which disturbed the weight measurement. A smaller solid style basket was then designed, weighing ~0.6 gm. (0.375 inch diameter). Experiments with this second basket

showed much more promise, with no evidence that the basket hit the sides of the reactor. The sides and bottom of the baskets were subsequently thinned with a file to reduce the weight of the basket further in order to reduce the thermal delay. After the filing process, the smallest solid basket used in this project weighed approximately 0.4 gm. This basket had a diameter of 0.375 in. and a height of 0.125 in.



Figure 4.2 Schematic of TGA baskets used for a) polyurethane and b) Removable Epoxy Foam.

The polyurethane samples were mainly analyzed in the baskets constructed from Incoloy mesh, since the polyurethane foam did not form any appreciable "flowing" phases throughout the degradation process. The solid style basket was used for the Removable Epoxy Foam because of the "liquid" or flowing phase formed during the degradation. Experiments at 1 bar and 10 bar were conducted **in** each basket with the polyurethane foam to determine the effect of basket type and size. The data from the mesh basket experiments were indistinguishable from the data collected using the smallest solid basket.

Sample Preparation

The samples of the polyurethane foam used in the decomposition experiments came in thin sheets, approximately 8" x 8" x 0.07". A circular punch was constructed to

obtain uniform samples. Each sample of the polyurethane foam was punched into a circle and then cut in half, with a diameter of 0.19 in., from a sheet with a thickness of 0.07 in. The sample sizes ranged from 2.0 mg. to about 6.5 mg.

The sample of the Removable Epoxy Foam came in a small block. Each sample of the Removable Epoxy Foam was thinly cut from the block so that the sample sizes ranged from 2.0 mg. to about 6.5 mg. The sample was cut to the thickness of the polyurethane foam samples (0.07 in.) The samples were more rectangular than circular due to the slicing process.

All samples were weighed on an independent micro-scale prior to analysis. Care was taken to ensure that dust and oils from fingers and other sources did not contaminate the sample. The samples were stored in small containers and kept at room temperature. The samples were also passed by a strip that emits alpha particles to reduce the static electricity built up during the punching or slicing process. The decrease in static electricity also allowed for better control of the samples as they were loaded into the baskets.

Test Variables

The important test variables previously determined by Sandia National Laboratories for foam decomposition are residence time, temperature, pressure and confinement. Different heating conditions were used to vary the temperature and residence time. Constant heating ramps of 10, 20 and 40°C/min were used, with maximum temperatures of 600°C. Isothermal conditions at 200, 300 and 400°C were also used. The for the isothermal conditions, the experiments started at room temperature,

were ramped at 20°C/min to the desired temperature, and then held at that temperature for approximately two hours. The pressure effects, with minimal confinement effects, can be measured in the high pressure thermogravimetric analyzer using various pressure conditions. Experiments were performed at reactor pressures ranging from 1 to 70 atmospheres. The experimental matrix used in this study is shown below in Table 4.1. The recoverable samples from each experiment were weighed and analyzed for elemental composition as outlined below.

		Pressure (atm)				
		1	10	30	50	70
Heating	10	Х				
Ramp	20	Χ	Х	Х	Х	Х
(°C/min)	40	Х				
Isothermal	200	Х				
Temperature	300	Х	Х			
(°C)	400	Х				

Table 4.1Experimental Matrix.

Gas Chromatograph

A Hewlett Packard 6890 series gas chromatograph was used to determine the concentration of the decomposition products from the polyurethane foam that leave the HPTGA. The current gas chromatograph setup uses a thermal conductivity detector. A calibration gas containing 96% helium, 1% hydrogen, 1% nitrogen, 1% carbon dioxide and 1% methane was used to quantify the concentration of the different products evolved from the foam samples. The main species of interest in the polyurethane foam decomposition experiment was carbon dioxide (CO₂). No CO₂ was detected during the

decomposition of the Removable Epoxy Foam. Hence, the gas chromatograph was only used during the polyurethane foam decomposition experiments.

The different species were separated through the use of a two-foot long, 1/8-inch diameter, stainless steel column filled with Carboxen® (Supelco 45/60 Carboxen 1000). This column separates organic molecules from inorganic molecules very easily. The data were analyzed through the use of Hewlett Packard ChemStation Rev. A.06.03 software and is explained in further detail in the next chapter. The concentration data were then related back to the corresponding degradation data.

Elemental Analysis

Mass fractions of carbon, hydrogen, nitrogen and sulfur in the foam samples were determined by a LECO 932 CHNS analyzer. Each sample was run through the analyzer five times. The sample sizes ranged from 0.8 to 1.2 mg. The mass fraction was found to vary less than $\pm 1\%$. The mass fraction of other elements (e.g. Si Al) can be determined through an ASTM ashing technique. In this technique, the sample is heated in an air environment to 750°C over a two-hour period and then held until the mass of the sample no longer changes. The organic components of the sample are oxidized, leaving only the heavier, less reactive components, called "ash". The ash commonly contains a very low percent of carbon, hydrogen, nitrogen, oxygen or sulfur. The most common elements in the ash are silicon and aluminum. Many other metals can be found in the ash. The oxygen mass fraction is then obtained by difference by subtracting the carbon, hydrogen, nitrogen, sulfur and ash from the total percent. The elemental data also serve as a way to evaluate the predicted elemental compositions for the parent and degraded foams.
Chapter 5. Experimental Results

The results from the various experiments with the HPTGA will be discussed in this chapter. A comparison of the different buoyancy effects observed will be presented first. A discussion of the analysis of the HPTGA data will be shown next, along with checks that were performed to ensure accuracy. The results from the thermogravimetric analysis of the polyurethane foam and the Removable Epoxy Foam are then given. Finally, results from the gas analysis from the degradation of the polyurethane foam are provided.

Buoyancy Effects

Buoyancy is very significant when weighing milligram-sized samples at elevated temperatures in the HPTGA. Buoyancy is defined as the force opposite gravity due to density gradients in this work. The buoyancy effects are defined as the effect of buoyancy on the microbalance weight measurement. Buoyancy is a strong function of both temperature and pressure, especially during heating and cooling ramps. The buoyancy effects were found to be a function of the inert atmosphere as well as the basket size. An accurate assessment of the buoyancy effects is important when obtaining a mass history. A shift in the curve due to buoyancy can change the calculated reaction rate coefficients. To account for the buoyancy effects, several experiments were conducted with an empty basket (blank experiments) at different conditions. The blank experiments were very repeatable. A representative set of blank experiments at 10 bar is shown in Figure 5.1. The blank experiments were performed with a mesh style basket in a nitrogen inert atmosphere in the reactor. An average of the blank experiments at each condition was used when determining the buoyancy effects.



 N_2 , mesh basket)

As seen in Figure 5.1, the blank experiment appears to have a nonlinear dependence to the temperature during a constant temperature ramp. This dependence is also observed when looking at the blank experiments at other pressures. The pressure dependence appears to be very close to linear for the blank experiments. Figure 5.2 shows the blank experiments normalized by the respective pressures. For example, the

blank response of the 50 bar blank experiment ends at 600° C at a weight of 0.4 mg / bar • 50 bar = 20 mg. When comparing the blank response to the average sample weight of 4 mg, it can be seen that the buoyancy effects are significant and need to be taken into account.



The atmospheric pressure blank experiments do not follow the same temperature dependence that the higher pressure blank experiments appear to follow. One possible explanation is that the decrease in the buoyancy effects near the end of the experiment is present in all of the blanks, but since the atmospheric pressure blank experiment is of the smallest magnitude, the effect is much more noticeable. This decrease in the buoyancy effect may be attributed to the thermal delay between the basket and the inert atmosphere.

When the inert atmosphere in the reactor was changed from nitrogen to helium, a dramatic decrease in the buoyancy effect was observed. The buoyancy effect seemed to decrease by an order of magnitude. This effect may be due to the decrease of the molecular weight of the carrier gas. The increase in the thermal conductivity was the primary objective when changing the inert atmosphere from nitrogen to helium, in order to insure that the sample temperature was as close as possible to the measured thermocouple temperature. The decrease in the buoyancy effects was somewhat unexpected. Figure 5.3 shows the difference in the blank experiments for the 1 bar and the 30 bar conditions as the inert atmosphere was changed.



Figure 5.3 Comparison of the average blank experiments at the 1 and the 30 bar conditions for the two inert atmospheres. (20°C/min, mesh basket)

The buoyancy effects were dramatically reduced when the inert atmosphere was changed from nitrogen to helium, as shown in Figure 5.3. The 30 bar condition shows that the blank response decreases by an order of magnitude as the inert atmosphere was changed. The initial increase in weight seen with the nitrogen is no longer observable when helium is the inert atmosphere for the 1 bar condition. Only the slow decrease is apparent. Although the change in the inert atmosphere decreased the buoyancy effects, they are still significant and need to be accounted for to obtain accurate pyrolysis data.

When analyzing the foam decomposition data (discussed in more detail in a later section), the blank experiment is subtracted from the data to obtain the true mass loss curve. As the magnitude of the blank response decreases, the effect of the variation from the blank response on the data decreases. For example, at the 50 bar condition with nitrogen, the blank response had a ~20 mg difference from the beginning to the end. Since the sample sizes ranged from 3-6.5 mg, the mass loss curve was obtained by subtracting ~20 mg from ~24 mg. If there were an error in the blank measurement, the effect would be much more dramatic than if helium was used as the inert atmosphere and the blank response was about 2 mg.

A difference in the blank experiments was observed when the basket size was changed. This is illustrated below in Figure 5.4 for blank experiments in helium. As observed in Figure 5.4, the blank response was more dramatic for the large solid basket. This could be from the large projected surface area of the basket. The projected surface area of the medium solid basket, small solid basket, and mesh cone basket were all about the same size, but were about 1/3 of the projected surface area of the large solid basket. The major difference between the medium and the small solid basket was the thickness of

the sides and bottom (versus diameter of the bottom) as discussed earlier. The primary goal of reducing the basket size was to reduce the thermal delay between the sample and the inert atmosphere, but the reduction in the blank response was an added effect.



Figure 5.4 Comparison of blank experiments with different basket styles. (1 bar, 20°C/min, He)

Data Reduction

To reduce the data obtained from the HPTGA, first the blank experiment for the same condition must be subtracted from the data to correct for buoyancy effects. The blank must be at the same temperature ramp, pressure, inert atmosphere, and basket configuration. Once the buoyancy effects were accounted for, the mass history of the sample was normalized by the initial mass for best comparison with duplicate experiments. However, due to degassing of adsorbed species at low temperatures, the initial mass changes slightly even at low temperatures. To allow for optimal comparison between the various experiments, the "degassed" mass was used to normalize the mass history. The procedure to obtain the "degassed" mass is:

- The initial "degassed" mass is estimated from the average value of the sample as it is heated from 75°C to 175°C (20°C/min).
- 2. Following the experiment, the reacted sample is removed from the HPTGA and re-weighed on an independent microbalance.
- 3. The final value of fraction of the initial sample remaining (m/m₀) is forced on the HPTGA data by changing the initial value of the "degassed" mass.

An example of this procedure is shown below. This foam sample had an initial mass of 2.240 mg measured on a microbalance. First, the blank for this experiment was subtracted, and the initial value was used to calibrate the scale. The percent of mass was calculated by dividing by the initial mass. The normalized mass versus temperature data for this experiment is shown in Figure 5.5.

A steady decrease in sample mass is observed as the sample was heated from 60° C to 75° C. At temperatures between 75° C and 200° C, the values seemed to plateau around 97%. When a sample is treated at 60° C for 5 minutes before starting the experiment, the same decrease is observed, with stabilization at about 97% of the original weight. Since the initial reading from the balance varied with time, the experiments were difficult to compare. In order to remove the influence of this initial degassing, the "degassed" mass was determined to be the average measurement between 75° C to 175° C.

When the data seen in Figure 5.5 are normalized by this "degassed" mass, the curve in Figure 5.6 is obtained.



microbalance.

At this point, the "degassed" mass has become 2.173 mg (~97% of the 2.240 mg used in Figure 5.5). However, the mass versus temperature data in Figure 5.6 does not quite match the final sample weight determined independently (step 2). For example, for this specific case, the final normalized mass remaining at 600°C in Figure 5.6 is 1.53%, as compared to 1.52% (determined on a separate balance using 2.173 mg as the "degassed" mass). Finally, the initial value of the "degassed" mass (at 75°C to 175°C) was adjusted to 2.174 mg to give an end weight percentage of 1.52% on the graph from the HPTGA, which matches the independent mass balance.



range from 75 °C to 175 °C.

Once three to eight comparable data sets for the various conditions were obtained, they were averaged together to give an overall percent mass history for the various conditions. The standard deviations of the data sets were also calculated. The upper and lower bounds of the data sets were assumed to be twice the standard deviation.

Data Confirmation

To insure that (a) the buoyancy effects had been correctly accounted for, (b) the data reduction scheme was correct, and that (c) the data from the HPTGA was accurate, two techniques were used. The first technique was to compare the HPTGA data with corresponding data collected on a different thermogravimetric analyzer (TGA) at Sandia

National Laboratories. Figure 5.7 shows a comparison of data collected at BYU from the HPTGA at atmospheric pressure and at Sandia from an atmospheric TGA for the Removable Epoxy Foam. The inert atmosphere in the HPTGA reactor was helium, while at Sandia, nitrogen was used. A heating ramp of 20°C/min was used in both experiments.



Figure 5.7 Comparison of mass history for Removable Epoxy Foam on two different experimental apparatuses. (20°C/min, 1 bar)

As seen in Figure 5.7, the data from the two separate experiments agree very well throughout the entire temperature range. This comparison was performed with the polyurethane foam and at different heating ramps as well. All the comparisons exhibited good agreement between the HPTGA data and the Sandia TGA data.

The next technique used to confirm the accuracy of the data used was to perform "partial" experiments of the conditions being tested. A "partial" experiment is an experiment that is stopped in the middle of an experiment to observe the intermediate behavior. The foam sample was then weighed and compared with the data from the complete experiment. For example, for the ramp experiments, the experiment was stopped at 320 or 350°C, instead of going to 600°C. For the isothermal experiments, the samples were removed after only 60 or 80 minutes. Figures 5.8 and 5.9 show the results from the partial experiments plotted versus the average and upper and lower limits for a ramp experiment and an isothermal experiment, respectively. The circles indicate where the experiments were stopped.



Figure 5.8 Illustration of how the partial experiments compare with the average and limits for a ramped experiment. (20°C/min, PUF, He, 1 bar)



Figure 5.9 Illustration of how the partial experiments compare with the average and limits for an isothermal experiment. (300°C, REF, He, 1 bar)

The resulting partially reacted foam was then weighed on an independent scale for further confirmation. As seen in Figures 5.8 and 5.9, the partial experiments agree very well within the upper and lower limits for both experiments. Good agreement between the partially reacted samples mass and mass measured on the HPTGA was obtained for all of the conditions tested and can be seen in Appendix B.

As illustrated by the two data confirmation techniques, the pyrolysis data collected on the high pressure thermogravimetric analyzer are reliable. The data collected at the same conditions on an independent thermogravimetric analyzer at ambient pressure agree very well with the data collected on the high pressure thermogravimetric analyzer. The partial experiments that were then weighed on an independent scale agreed very well with the full experiments. These two techniques seem to be capable of showing the reliability of the high pressure thermogravimetric analyzer data corrected for buoyancy effects.

Pyrolysis Experiment Results

With confirmation that the data collected are accurate, the averages of three to eight experiments for each condition can be shown. Figures 5.10 and 5.11 show the results of the various heating ramps tested for the polyurethane foam and Removable Epoxy Foam, respectively.



Figure 5.10 Mass history for various heating ramps for polyurethane foam. (1 bar)

As seen in Figure 5.10 and 5.11, as the heating rate was increased, the mass history shifted to the right for both the polyurethane foam and the Removable Epoxy Foam. For

both foams, the shape of the curve did not change very much as the heating rate was increased. For the polyurethane foam, there appears to be a shift in the mechanism of decomposition at a temperature of about 350°C, as indicated by a knee in the curve. For the Removable Epoxy Foam, the mass loss curve is very different than for the polyurethane foam. There appear to be multiple decomposition steps. At 150°C the mass loss curve drops dramatically to ~85% of the initial sample mass, and then slowly decreases. At 230 and 340°C the slope of the mass loss curve increases. At 500°C the slope decreases, until at 600° C the sample is only ~5% of the initial sample mass.



(1 bar)

As seen in Figure 5.10, the mass loss curve shifted 10°C higher as the heating rate was increased from 10 to 20°C/min for the polyurethane foam. The mass loss curve

shifted 5°C higher as the heating rate was increased from 20 to 40° C/min. As seen in Figure 5.11, the mass loss curve shifted 15°C higher as the heating rate was increased from 10 to 20° C/min for the Removable Epoxy Foam. The mass loss curve shifted 10° C higher as the heating rate was increased from 20 to 40° C/min.

The pressure effect on the decomposition in the absence of confinement effects for the polyurethane foam and the Removable Epoxy Foam is shown in Figures 5.12 and 5.13, respectively. The data shown are an average of the experiments at the various pressures. The experiments were all conducted at a constant heating ramp of 20° C/min in helium.



Figure 5.12 Mass history versus pressure for polyurethane foam. (20°C/min)

As the pressure increases, the mass history of both foams shifts to higher temperatures, indicating that a higher temperature was required to vaporize the decomposition products. This matches the theory that the vaporization depends on both the vapor pressures of the products as well as the ambient pressure. As seen in Figure 5.12, the mass loss curve shifted 10°C higher as the pressure was increased from 1 to 10 bars for the polyurethane foam. The shift increased to 20°C as the pressure was increased to 30 bar. The mass loss curve was shifted 40°C higher with either a pressure of 50 or 70 bar. The data collected at 70 bar are statistically indistinguishable from the 50 bar data for the polyurethane foam. Also, the shift in the mechanism for the polyurethane foam apparently disappears as the pressure increased.



As seen in Figure 5.13, the mass loss curve shifted 20° C higher as the pressure was increased from 1 to 10 bars for the Removable Epoxy Foam. The mass loss curve was shifted 40° C higher with either a pressure of 30 or 50. Data collected at 50 bar are

statistically indistinguishable from the 30 bar data for the Removable Epoxy Foam. Furthermore, the change in the slope of the decomposition appears to be shift to a lower temperature with increasing pressure.

In addition to the ramped experiments shown above, several isothermal experiments for both the polyurethane foam and the Removable Epoxy Foam were conducted. The results are shown in Figures 5.14 and 5.15. The isothermal data shown were also corrected for the blank behaviors and the data shown are the average of three to five experiments.



Figure 5.14 Mass history for various isothermal polyurethane foam experiments.

The isothermal experiment at 200°C showed very little degradation of the foam for the polyurethane foam. The foam degraded to ~23% of the initial sample as the temperature increased to 300° C. The degradation increases such that only ~1% of the

initial sample is left after 2 hours when the temperature is increased to 400° C. This matches the degradation seen in the 20° C/min heating ramp experiments to 600° C. When the 300° C isothermal experiment was conducted at 10 bar instead of 1 bar, the mass history was shifted about 10% of the initial sample higher throughout the entire experiment. In other words, the mass loss in the 10 bar, 300° C experiment is about 10% less than the mass loss for the 1 bar, 300° C experiment at all times.



Figure 5.15 Mass history for various isothermal Removable Epoxy Foam experiments.

The isothermal experiment at 200°C leveled off at ~80% of the initial sample after 2 hours for the Removable Epoxy Foam. The initial drop off at 150° C was still apparent for all of the isothermal experiments. The foam degraded to ~45% of the initial sample when the temperature was increased to 300° C. The degradation increased until ~11% of

the initial sample remained after 2 hours when the isothermal experiment was conducted at 400° C. The ~11% remaining in the 400° C experiment is about twice the percent of the initial sample that remained at the end of the 20° C/min heating ramp experiments to 600° C. When the 300° C isothermal experiment was conducted at 10 bar instead of 1 bar, the mass history was shifted about 10% of the initial sample mass higher throughout the entire experiment, like the polyurethane foam.

Gas Chromatograph Data

Gas chromatograph data were only collected during the decomposition of the polyurethane foam. The gas chromatograph was set up to detect carbon dioxide. Since very little carbon dioxide was detected from the decomposition of the Removable Epoxy Foam, the gas chromatograph was not used during those experiments. Carbon dioxide was determined to be one of the major decomposition products of the polyurethane foam. Carbon dioxide was detected during the second half of the experiments, after the apparent shift in the mechanism, through analysis of the decomposition gases from the TGA at Sandia National Laboratories (Hobbs et al., 1999; 2000). Furthermore, the amount of carbon dioxide produced as a decomposition product increased as the orifice size was decreased. To determine if this effect occurred with increasing pressure as well, the gas chromatograph was used with the HPTGA.

The raw data from the gas chromatograph were manipulated to obtain the cumulative and instantaneous percentage of the polyurethane foam that was released as carbon dioxide. The procedure used to manipulate the raw data is described below. First, the area under the carbon dioxide peaks (A, mV·min) was found using the ChemStation

Rev.A.06.03 software. Manual integration allowed for an accurate and consistent value. An example of a typical spectra is shown below in Figure 5.16. The area under the peaks was calculated by drawing a base line on the spectra (as shown by the dotted lines in Figure 5.16), and integrating to obtain the area under the curve. In this example, the first peak area is 4.42 mV·min, while the area for the second peak is 0.265 mV·min. The first peak represents the residual nitrogen in the gas, while the second peak is the carbon dioxide. The lines were drawn manually to ensure comparable results.



Figure 5.16 Example spectra of the off gases from the HPTGA.

The area was then converted to a concentration through a calibration factor (cal,

 $\frac{mg}{L \cdot mV \cdot \min}$). For the current settings of the gas chromatograph, the calibration factor

was found to be $0.039 \frac{mg}{L \cdot mV \cdot \min}$, through the use of a calibration gas. The

concentration was then multiplied by the total flowrate (Q, L/min) in the HPTGA to give a rate of carbon dioxide release. The mass release of carbon dioxide per time for each experiment was then divided by the initial mass (m0, mg) to obtain a percent mass release as carbon dioxide per time (%/t, percent/min). This procedure is given in Equation 5.1:

$$\%/t = A \cdot cal \cdot Q/m0 \tag{5.1}$$

The discrete rates were linearly interpolated to provide a continuous function for integration. The rate curve was then integrated for a cumulative percent mass release. Several different experiments were performed and each cumulative percent mass release was then averaged together to give the final average percent mass release per time for each pressure. There was considerable standard deviation between the different experiments, which was most apparent in the last 1/3 of the experiment. This was most likely caused by the cumulative nature of the mass release per time error. An example of the spread in results is shown below in Figure 5.17. Even with eight or more separate experiments, the standard deviation did not decrease.

One method found that reduced the standard deviation was a normalization technique. During the analysis, even though the inert atmosphere was helium, there was still a trace amount of nitrogen that appeared as a peak. The area of this peak was fairly constant during the experiment. It was noticed, however, that as small increases in the pressure occurred, the area under the nitrogen peaks would decrease slightly. This can be observed in Figure 5.18.



Figure 5.17 Eight replicates for a 20°C/min temperature ramp at 1 bar pressure condition.



Figure 5.18 Comparison of pressure in HPTGA and nitrogen peaks from gas chromatograph during a 20°C/min temperature ramp at 30 bar condition.

The carbon dioxide peaks were then normalized by multiplying by the ratio of a) the first nitrogen peak (before the pressure fluctuations occurred) to b) the peak for nitrogen at the same point. This method assumes that the pressure fluctuations have the same relative effect on the nitrogen to carbon dioxide peaks. Since the amount of nitrogen still contained in the reactor varied from experiment to experiment, the initial value from each separate experiment was used for the normalization. This normalization only modified the end results by less than 5%.

An additional constraint to the data reduction procedure was to limit the maximum mass release for carbon dioxide per time to the total mass release at the same point. This helped to eliminate any extraneous data points from the linear interpolation. This limitation was only effective in the temperature zone of 450-600°C (in the ramped experiments), when the total mass release rate was low.

Data were only collected for the temperature ramp condition for pressures lower than 30 bar and for the isothermal condition at one bar. As pressure increased, the concentration of carbon dioxide in the effluent decreased. The signal to noise ratio was too low for a good reading at the higher pressure conditions. The carbon dioxide release was so slow that the effluent concentration was below the gas chromatograph measurement threshold at higher pressures for the isothermal condition.

After normalizing each experiment with the nitrogen peaks, and taking the average and standard deviation for each pressure, at a temperature ramp of 20°C/min, Figures 5.19 and 5.20 were produced. Figure 5.19 shows the cumulative percent of the initial sample that was released as carbon dioxide, while Figure 5.20 shows the rates on a

69

percent of the initial sample basis. The standard deviations shown in Figure 5.19 are the standard deviations at 575-600°C.



Figure 5.19 Average cummulative CO₂ release of experiments for 20°C/min temperature ramp at various pressure conditions.

From Figure 5.19, it appears that as pressure increases, the amount of sample released as carbon dioxide also increases. It also appears that the amount of sample released as carbon dioxide decreased slightly when the pressure increased from five to ten bar. The standard deviations for the five and ten bar experiments are $\pm 1.95\%$ and $\pm 2.4\%$, respectively. The difference between these two experiments is only 1%, and so the apparent decrease may be due to noise. The differences between the 30 bar experiment and the other pressure conditions are definitely outside of the standard deviation limits for the one, five and ten bar conditions.



Figure 5.20 Average carbon dioxide production rates for the various pressure experiments.

From Figure 5.20, it appears that the carbon dioxide production becomes the major part of the mass released at one bar after the temperature has reached $\sim 410^{\circ}$ C. The temperature at which the major part of the mass released is carbon dioxide increases to $\sim 475^{\circ}$ C as the pressure increases to 30 bar. These data support the conclusion that a shift in the mechanism occurs at increased temperature. These data also support the conclusion that this shift does change with pressure.

The data collected during the isothermal 300°C experiments is shown below in Figure 5.21 and compared with the atmospheric 20°C/min data. From Figure 5.21, it can be seen that the 300°C isothermal condition gives off carbon dioxide in a different manner than the ramped experiments. The release is much slower, due to the lower temperatures. Furthermore, it appears that more carbon dioxide could be released if the

experiment was allowed continue even further. This is especially apparent when the amount of decomposition is considered. After the ramped experiments only $\sim 2\%$ of the initial sample remained, while after the isothermal experiments $\sim 23\%$ of the sample remained. Yet the total percent of the sample released as carbon dioxide is within $\sim 2\%$ for both cases.



Figure 5.21 Average of experiments for 1 bar pressure, 20°C/min temperature ramp condition and 300°C isothermal condition.

The decomposition of the polyurethane foam and the Removable Epoxy Foam are dependent on the heating rate, pressure and confinement. As the heating rate, pressure and confinement increase, the mass loss curves shift to the right (i.e. less decomposition at the same time/temperature). For the polyurethane foam, as the pressure increased, an increase in the carbon dioxide produced was observed. This is similar to the increase in carbon dioxide produced as the orifice size decreases. These data quantify the heating rate, pressure and confinement effects on the foam decomposition.

Chapter 6. Modeling Approach

The general approach used in the foam decomposition model is discussed first in this chapter. The chemical mechanism used for the polyurethane foam decomposition model is presented next. Finally, the rate equations associated with the chemical mechanism and how they are integrated are shown.

General Approach

The current approach used to develop the thermal degradation model for the polyurethane foam is a modified version of the CPD (Grant et al., 1989) and CPUF (Hobbs et al., 1999; 2000) models to include flow in and out of the computational cell. The majority of the model will be directly applicable for the Removable Epoxy Foam as well. Both the CPD and CPUF models (discussed earlier) were originally developed as batch reactors for one cell. The CPD model considered one coal particle as the cell, while the CPUF model was applied to one grid cell at a time. However, in order to incorporate the effect of flow (and hence confinement) for the cell, a continually-stirred reactor (CSTR) approach must be used. This major difference between a batch reactor and a continually-stirred reactor can be seen in the overall and species continuity equations. The overall mass balance and the mass balance for species i in a continually stirred reactor are shown below:

$$\frac{dM_{tot}}{dt} = \dot{M}_{tot}^{in} - \dot{M}_{tot}^{out}$$
(6.1)

$$\frac{dM_i}{dt} = \dot{M}_i^{in} - \dot{M}_i^{out} + \dot{M}_i^{gen}$$
(6.2)

The "in" and "out" terms in both the overall and the species mass balances are not included in a batch reactor approach. The terms on the right-hand side of both equations are functions of time. The time dependence of each term must be calculated to use this equation to model the time dependence of the overall mass and the mass of species i in the control volume.

Four test cases were considered while developing the continually-stirred reactor approach, which correspond to the different data sets that were collected. These cases are referred to as unconfined, partially-confined, totally-confined, and general. Different inlet and outlet flow conditions exist for the different cases, but the reactions that can take place are the same. The unconfined case refers to a sample that is allowed to react as a continuous stream of inert gas passes by, in essence removing the generated species from the reaction zone. The partially-confined case refers to a sample that is enclosed in a metal basket with a small orifice in the lid. The pressure rises as the sample reacts. More gas will flow through the orifice as the pressure rises. The totally-confined case refers to a sample enclosed in a totally-confined cell, in which the pressure generated by the sample was measured as more and more gas was generated. The general case is where the inlet flow could contain any distribution of the possible species from a neighboring cell. This case could also have a condensed phase flowing in or out of the cell as well. The reactive species flowing into the cell are calculated from the reactive species flowing out of the neighboring cells. The general case is the broadest case, and is the case for

which the model was designed. The other cases are simplifications of the general case. A table of the inlet and outlet conditions for each case is shown below. (Table 6.1)

Case	Unconfined	Partially- confined	Totally- confined	General
Inert in	Х	Х		Х
Reactive Species in				Х
Pressure Change		Х	Х	Х
Flowout	Х	Х		Х

Table 6.1Inlet and outlet conditions for various cases.

The solution algorithm of the decomposition model is divided into three steps:

- 1. Numerical integration of the kinetic expressions for the bridge reactions.
- Calculation of the mass of each species generated from the bridge reactions through percolation lattice statistics.
- 3. Calculation of the inlet and outlet mass flow for each species, along with the distribution of the species in the vapor/liquid/solid phase.

These three steps correspond to the three steps in the original CPD model and are shown in a simple form in Figure 6.1. Although the model is divided into these three steps, the terms in the differential equations are all calculated simultaneously and used together. Each step of the model will be discussed in further detail. Step 1 is discussed in this chapter, while steps 2 and 3 are discussed in the following chapters. A final summary of the equations used in the model will then be shown in Chapter 9, along with a discussion of the parameters that were used in the equations.



Figure 6.1 Representation of the sequence of calculations for the thermal degradation model.

Chemical Mechanism

The first procedure in establishing a decomposition model based on percolation lattice statistics is to classify parts of the foam molecule into sites, bridges and side chains. In the percolation lattice statistics approach, the polymer is viewed as an infinite array of sites, bridges and side chains. A "site" is defined as the portion of the polymer that can be isolated by bridges or side chains, and stays intact and does not react during the pyrolysis. A "bridge" is a series of molecules that connect one site to another site. As the bridges react, they form "side chains" and "light molecules". A side chain is a former bridge that is now only connected to one site and then terminates. A light molecule is a former side chain that has been totally severed from the site. A representation of the various parts of a polymer molecule is shown in Figure 6.2.



Figure 6.2 Representation of a simple polymer molecule showing sites, bridges, side chains and light molecules.

When dividing the polymer into sites, bridges and side chains, certain criteria must be observed to insure that the percolation lattice statistics are applicable. The sites should be chosen such that they do not change or react during the reactions. The site may be as small as a single carbon with one bond as long as it is always a single carbon with one bond throughout the degradation process. The only stipulation when designating bridges is that they are only connected to two sites. The statistics were based on the assumption that a bridge has only two connection points. A side chain must only be attached to a single site within the representation. The breakdown of the initial polyurethane foam structure into sites, bridges and side chains is shown in Figure 6.3 using the three most common structures for the polyurethane foam.



Figure 6.3 Breakdown of the three most common structures of the polyurethane foam into sites and bridges.

As seen in Figure 6.3, there are two different site types, two different bridge types and no side chain types in the initial structure of the polyurethane foam. The most common site type (Site-1) is the propane backbone of the trimethylolpropane. This was chosen as a site since the carbon oxygen bond just after the propane backbone was assumed to be the bond that is broken during the decomposition. The trimethylolpropane was also set apart as a site because it was connected in three locations. For the same reason, the two carbons with the oxygen in the middle of the diethylene glycol were chosen as the second type of site (Site-2). The most abundant bridge type (Bridge-1) has two urethane linkage structures. The bridge includes every atom between the two sites. The other bridge type (Bridge-2) is an adipate bridge. This was denoted as a bridge because it is also located

between two sites and is very reactive. No side chains were depicted in Figure 6.3 since there were no reactive terminating molecules that are attached to a site.

The next procedure in composing a decomposition mechanism is to determine how the bridges will react to release the observed decomposition products. For the polyurethane foam, the main decomposition products that were observed are toluene diisocyanate (TDI), toluene diamine (TDA), carbon dioxide (CO_2) and cyclopentanone (CPN). Many C₅ and C₆ products were also detected (Hobbs et al., 1999; 2000). The urethane linkage type bridges appear to be the most likely source of the TDI, TDA and CO_2 , whereas the cyclopentanone most likely came from the adipate bridges. The C₅ and C₆ structures most likely came from the trimethylolpropane sites after the bonds were broken and smaller side chains were generated.

Another feature of the decomposition mechanism that should be considered during development is how the bridges react. To be consistent with the lattice statistics, when a bridge breaks, two side chains must be formed. A bridge must be formed from two side chains. One of the side chains can be as small as a hydrogen molecule or even an electron forming a radical species. The bridges or side chains can react to give off light molecules, but they cannot change the stoichiometric coefficient of the reactions. For example, a bridge can give off a light molecule and then become a different bridge. The main idea is that the stoichiometric coefficient between the bridges and side chains remains constant (i.e. two side chains came from one bridge). Furthermore, the side chains can react further to produce light molecules, but a smaller side chain must always remain to keep the stoichiometric coefficient of bridges to side chains constant. Again, if necessary, the side chain may be as small as a hydrogen molecule, or even an electron with essentially zero mass. Also, a bridge may be as small as a single bond between two sites. This bridge would have an effective mass of zero. Care must be taken, when one of the species has an effective mass of zero. The division by zero in the calculations can lead to numerical errors in the results.

A reaction scheme was developed, in collaboration with Sandia National Laboratories, which generates the majority of the observable decomposition products, and is shown below in Figures 6.4 and 6.5. The symbols defined in Figure 6.4 are used in the condensed version seen in Figure 6.5.

As seen in Figures 6.4 and 6.5, as the bridges break into various parts, many species are generated. The di-urethane bridge (L_1) , breaks into a urethane-isocyanate side chain (D_1) , and a hydroxyl side chain (D_2) in reaction 1. Reaction 2 is the reverse of reaction 1. Reaction 3 has the other urethane linkage breaking into an isocyanate group and a hydroxyl group, forming another hydroxyl side chain and a toluene diisocyanate (TDI). Reaction 4 involves the reattachment of the toluene diisocyanate with a hydroxyl side chain to form a urethane-isocyanate side chain. The di-urethane bridge releases a carbon dioxide molecule (CO_2) and forming a smaller urethane-amine bridge (L_2) in reaction 5. Reaction 6 show the urethane-amine bridge breaking to form an isocyanate group and a hydroxyl group, similar to reactions 1 and 3, and forming a hydroxyl side chain and a isocyanate-amine side chain (D_3) . Reaction 7 is the reverse of reaction 6. The urethane-amine bridge releases another carbon dioxide molecule to generate a diamine bridge (L_3) during reaction 8. Reaction 9 shows the severing of the diamine bridge into a diamine side chain (D_4) and a CH_2 radical side chain (D_5) . Similarly, reaction 10 shows the severing of the diamine side chain forming another CH₂ radical
side chain and a toluene diamine molecule (TDA). The adipate bridge (L_4) is split into a CH₂ radical side chain, a carbon dioxide molecule, a cyclopentanone molecule (CPN), and a CH₃O radical side chain (D_6) in reaction 11.



Figure 6.4 Illustration of the major decomposition reactions for the polyurethane foam.



Figure 6.5 Condensed illustration of the reaction pathways for the polyurethane foam decomposition.

These reactions are not the elementary reactions that take place during the bridge reactions, but rather the overall reactions for the various steps. In reactions 9, 10 and 11, radical species are generated. These species eventually extract a hydrogen molecule from somewhere in the foam or recombine. The hydrogen extraction reactions were not explicitly defined because there are many possibilities for where the hydrogen molecule came from. Illustrating the majority of those possibilities would greatly increase the number of reactions. The reaction scheme was kept as small as possible while generating the major products.

Solution of Rate Equations

The purpose of the first step of the model is to numerically integrate the kinetic rate expressions. The kinetic rate expressions are integrated using a backward difference solver. The DDEBDF solver (Shampine and Watts, 1979) was used, since it is very efficient in solving stiff problems. This solver uses the backward difference formulas of

orders one through five to integrate a system of first-order ordinary differential equations over a specified time step. The solver takes several (up to 1000) intermediate steps to then obtain the number of bridges, side chains, and light molecules that are present after a designated time step.

Kinetic expressions are developed for the formation and disappearance of bridges, side chains and light molecules. Population variables (i.e. normalized number densities) are used in the rate expressions due to their intrinsic nature. The number densities were calculated from the mass and the molecular weight of the species and then divided by the volume of the computational cell, as shown below in Equation 6.3.

$$N_i = \frac{M_i}{MW_i \cdot V_{cell}} \tag{6.3}$$

The population of species i is then calculated by dividing the number density of species i by the total initial number density of the similar species. For example, the population of bridge type one (L_1) is calculated by dividing the number density of bridge type one (N_{L_1}) by the total initial number density of all the bridges (N_T^{bridge}) as seen in Equation 6.4.

$$L_1 = \frac{N_{L_1}}{N_T^{bridge}} \tag{6.4}$$

The population variables increase and decrease due to both flow and reaction. The population variables can even increase to a number greater than one. For example, if a lot of the bridge type one molecules were to flow into the computational cell, the number density of bridge type one would increase. If enough of bridge type one were to flow into the cell, the number density of the bridge type one could be greater than the initial number density of all of the bridges, generating a population of bridge type one greater than one. The population is directly proportional to the mass of the species. The population variables are never less than zero, since that would correspond to a negative mass.

Table 6.2 shows the overall rate equations from the chemical mechanism denoted in Figures 6.4 and 6.5.

Table 6.2Rate equations for the various species in the polyurethane foam
decomposition.

Species	Overall Rate Equations
L_1	$\frac{dL_{1}}{dt} = -k_{1} \cdot L_{1} + k_{2} \cdot D_{1} \cdot D_{2} - k_{5} \cdot L_{1}$
L_2	$\frac{dL_2}{dt} = +k_5 \cdot L_1 - k_6 \cdot L_2 + k_7 \cdot D_2 \cdot D_3 - k_8 \cdot L_2$
L_3	$\frac{dL_3}{dt} = +k_8 \cdot L_2 - k_9 \cdot L_3$
L_4	$\frac{dL_4}{dt} = -k_{11} \cdot L_4$
D_1	$\frac{dD_1}{dt} = +k_1 \cdot L_1 - k_2 \cdot D_1 \cdot D_2 - k_3 \cdot D_1 + k_4 \cdot TDI \cdot D_2$
<i>D</i> ₂	$\frac{dD_2}{dt} = +k_1 \cdot L_1 - k_2 \cdot D_1 \cdot D_2 + k_3 \cdot D_1 - k_4 \cdot TDI \cdot D_2 + k_6 \cdot L_2 - k_7 \cdot D_2 \cdot D_3$
D_3	$\frac{dD_3}{dt} = +k_6 \cdot L_2 - k_7 \cdot D_2 \cdot D_3$
D_4	$\frac{dD_4}{dt} = +k_9 \cdot L_3 - k_{10} \cdot D_4$
D_5	$\frac{dD_{5}}{dt} = +k_{9} \cdot L_{3} + k_{10} \cdot D_{4} + k_{11} \cdot L_{4}$
D_6	$\frac{dD_6}{dt} = +k_{11} \cdot L_4$
TDI	$\frac{dTDI}{dt} = +k_3 \cdot D_1 - k_4 \cdot TDI \cdot D_2$
TDA	$\frac{dTDA}{dt} = +k_{10} \cdot D_4$
CPN	$\frac{dCPN}{dt} = +k_{11} \cdot L_4$
<i>CO</i> ₂	$\frac{dCO_2}{dt} = +k_5 \cdot L_1 + k_8 \cdot L_2 + k_{11} \cdot L_4$
* w	where $k_i = A_i \cdot \exp\left(-\frac{E_i}{R_g} \cdot T\right)$

The k's represent the rate constant for the specific reaction. The rate constants are of the standard Arrenhius form, as shown at the bottom of the table. The rate equations all have a first order dependence on the population of the various species. All rate coefficients were determined empirically from the data in this work. This process is discussed in more detail in Chapter 9.

With the polyurethane foam decomposition mechanism and rate equations established, the main portion of the MTPUF model can be described. The equations and techniques set forth in the future chapters are not unique to the polyurethane foam decomposition mechanism. For example, it is anticipated that a decomposition mechanism for Removable Epoxy Foam will be developed at Sandia National Laboratories. As long as the foam can be described as sites, bridges, side chains and light molecules, these techniques will still be applicable. The use of the polyurethane foam decomposition mechanism therefore serves as an initial case for testing the MTPUF model.

Chapter 7. Lattice Statistics / Population Balance Theory

The percolation lattice statistics, briefly reviewed in Chapter 2, will be discussed in more detail in this chapter. A few of the characteristics observed while implementing the percolation lattice statistic are also shown. The benefits and limitations of percolation lattice statistics are discussed next. Finally, the population balance theory developed to enhance the capabilities of the percolation lattice statistics is explained.

Extended Percolation Lattice Statistics

The lattice statistics used in this model are adapted from the CPD model (Grant et al., 1989) as discussed earlier. The statistics have been expanded to incorporate multiple site, bridge, side chain, and light molecule types. Side chains, and light molecules are generated as the bridges break down during the reactions. Furthermore, smaller fragments (called oligomers) are generated as the bridges break. The number of sites contained within the oligomer structure indicates the size of the oligomers. Oligomers with one site are designated as monomers, while oligomers with two sites are designated as dimers, and so on. The mass of each oligomer can be calculated through percolation lattice statistics.

Species Mass

The oligomer containing n sites (n-mer) with no "loop" structures will always contain n-1 or s bridges and n(s-1)+2 or t side chains (Fisher and Essam, 1961). The molecular weight of the n-mer (MW_n) can then be calculated from the site (MW_{sit}) , bridge (MW_{brg}) , and side chain (MW_{sch}) molecular weights as follows:

$$MW_n = n \cdot MW_{sit} + s \cdot MW_{brg} + t \cdot MW_{sch}$$

$$\tag{7.1}$$

The first term in Equation 7.1 represents the number of sites (n) in the n-mer multiplied by the site molecular weight. The second term represents the number of bridges (s) in the n-mer multiplied by the bridge molecular weight. The third term represents the number of side chains (t) in the n-mer multiplied by the side chain molecular weight. For the case when there are multiple site, bridge and/or side chain types, the molecular weights used should be population-weighted (number-weighted) molecular weights of the sites, bridges and/or side chains. The result is then the number-weighted average molecular weight of the oligomer.

The differential material balance equations involve the total mass of the n-mer in the computational cell. The total mass of an n-mer (M_n) is obtained as follows. Since the sites are chosen such that they remain unchanged during the decomposition process, sites provide a convenient basis for converting from population variables to mass variables. Let m_n denote the total mass of the n-mer divided by the total number of sites, and let Q_n the n-mer population divided by the total number of sites. The term m_n is given by:

$$m_n = M W_n Q_n \tag{7.2}$$

where

$$Q_n = F_n / n = b_n p^s (1 - p)^t$$
(7.3)

and MW_n is given by Equation 7.1. The n-mer population on a per site basis (Q_n) is based solely on the fraction of intact bridges (p) and the coordination number (s + 1). The probability (F_n) that a given site is a member of a cluster of n sites with *s* bridges was defined previously in Equation 2.14 as:

$$F_{n}(p) = nb_{n}p^{s}(1-p)^{t}$$
(2.14)

The equation for nb_n was defined previously in Equation 2.16 as:

$$nb_{b} = \frac{\mathbf{s}+1}{s+t} \binom{s+t}{s} = \frac{\mathbf{s}+1}{n\mathbf{s}+1} \binom{n\mathbf{s}+1}{n-1}$$
(2.16)

with the binomial coefficient given for non-integer indices \mathbf{m} and \mathbf{h} defined previously in Equation 2.17 as:

$$\binom{\boldsymbol{m}}{\boldsymbol{h}} = \frac{\Gamma(\boldsymbol{h}+1)}{\Gamma(\boldsymbol{m}+1)\cdot\Gamma(\boldsymbol{h}-\boldsymbol{m}+1)}$$
(2.17)

where Γ is the standard gamma function. Here, non-integers arise from fractional values for s + 1, which might be interpreted as average values for lattices with mixed coordination numbers.

The mass of the n-mer on a per site basis (m_n) must be converted to the total mass of the n-mer (M_n) in the system for use in the differential equations. One technique used in percolation lattice statistics is to calculate the average mass per site for the system. Calculating the molecular weight of an extended site is one way to calculate the average mass per site for the system. An extended site includes the site and any bridges or side chains associated with the site. Since a bridge connects two sites together, only one half of the bridge is associated with each site. Since the population variables are on a per bridge basis, they are converted to a per site basis by multiplying by a factor of (s + 1)/2. The (s + 1)/2 factor is derived from the fact that for every site there are s + 1 bridges, but since each bridge is connected to two sites, there are (s + 1)/2 bridges per site. The mass of an extended site (m_{site}) is:

$$m_{site} = MW_{sit} + p \cdot MW_{brg} \cdot \frac{(\mathbf{s}+1)}{2} + (1-p) \cdot MW_{sch} \cdot (\mathbf{s}+1)$$
(7.4)

The fraction of intact bridges (p) is used to calculate the distribution of the attachments between the intact bridges and side chains. The first term in Equation 7.4 represents the mass associated with the site. The second term represents the mass associated with the bridges, while the third term represents the mass associated with the side chains. The $\frac{1}{2}$ factor is not present in the third term because each side chain is only connected to one site and so is not shared with another site. Again, if there are multiple site, bridge and/or side chain types, the population-weighted (number-weighted) averages of the molecular weights should be used. The mass of an extended site is the same as the total polymer mass divided by the total number of sites. The total polymer mass includes the masses of the n-mers as well as the infinite matrix, but excludes the masses of the light molecules and any other species (e.g., inert gas, etc.)

The total mass of the n-mer in the computational cell (M_n) is then calculated by multiplying the ratio of the initial total mass of the polymer to the initial mass of the extended site (M_p^0/m_{site}^0) by the total mass of the n-mer per site (M_p) , as follows:

$$M_{n} = m_{n} \cdot M_{p}^{0} / m_{site}^{0}$$
(7.5)

The initial values are used since the ratio of the total polymer mass and the mass of the extended site remains constant throughout the entire experiment. This ratio can be interpreted as a conversion factor between a total mass basis and a population per site basis.

The mass of the infinite matrix can be calculated from a simple mass balance with the masses of the polymer fragments calculated. The mass of an extended site includes the per site masses of all of the n-mers and the per site mass of the infinite matrix, based on percolation lattice statistics (Equation 7.4). Therefore, the per site mass of the infinite matrix (m_{inf}) can be calculated by the difference between the mass of an extended site (m_{site}) and the summation of the n-mer masses per site (m_n) :

$$m_{\rm inf} = m_{site} - \sum_{n} m_n \tag{7.6}$$

The total mass of the infinite matrix in the computational cell (M_{inf}) can then be calculated in a manner similar to Equation 7.5:

$$M_{\rm inf} = m_{\rm inf} \cdot M_p^0 / m_{site}^0$$
(7.7)

Similarly, the total mass of light molecule (such as TDI, TDA, CPN, or CO₂) type i (M_{I_i}) is calculated from the population on a per bridge basis of light molecule type i (I_i) and the molecular weights of light molecule type i (MW_{lm_i}) using the following equation:

$$M_{I_i} = I_i \cdot MW_{lm_i} \cdot \frac{s+1}{2} \cdot M_p^0 / m_{site}^0$$
(7.8)

The molecular weights of the light molecules are usually given by their structures. The population of the light molecules is multiplied by the (s + 1)/2 factor since the M_p^0/m_{site}^0 term is on a site basis and the light molecule population is on a per bridge basis.

Numerical Characteristics

There are some very interesting numerical characteristics that are apparent when the percolation lattice statistics are implemented. This arises from the fact that it is very inefficient to keep track of the infinite number of possible fragments that can be generated during the bridge reactions. A common numerical practice used while implementing percolation lattice statistics is to assume that large oligomers have similar properties to the infinite matrix. A cut-off point (n_{max}) is used to limit the number of oligomers considered in the calculations. One of the main factors used in determining n_{max} is the molecular weight of the n_{max} -mer. If the molecular weight is high enough, there is very little chance that it will vaporize, even at high temperatures. A large oligomer is more likely to break down into smaller pieces (e.g. from the infinite matrix to finite fragments) before it vaporizes. Other properties, such as viscosity, density, conductivity, etc., can also be considered when determining the cut-off point.

Treating large oligomers as part of the infinite matrix affects the shape of the $F_{inf}(p)$ versus p curve. The $F_{inf}(p)$ curve is the fraction of sites contained in the infinite matrix as a function of the fraction of intact bridges (p) and is one minus the F(p) seen in Figure 2.11. Figure 7.1 shows an example for a coordination number of three, where the oligomer sizes from six and larger are grouped with the infinite matrix.



Figure 7.1 Distribution of various oligomer sizes as a function of the fraction of intact bridges (p). (s+1=3, n_{max}=5)

When no n_{max} is used, the curve for the infinite matrix should drop dramatically to zero at a p = 0.5 (see Figure 2.11). In contrast, the infinite matrix curve asymptotically approaches zero as p approaches zero in the case illustrated in Figure 7.1. This gives the appearance that the infinite matrix exists throughout all values of p, which would correspond to a p_{crit} of zero. This pseudo- p_{crit} , or the apparent p_{crit} , will always be equal to zero if the cut-off point technique is used.

Figure 7.2 shows how the F(p) curve changes as more oligomer sizes are taken into account in the calculations. The F(p) curve is the sum of all the finite fragement and is equal to $1-F_{inf}(p)$. Again, a coordination number of three was used in this example.



Figure 7.2 Comparison of F(p) curves for various cut-off points (s+1=3).

As seen in Figure 7.2, when $n_{max} = 10$ (i.e. more terms are added), the value of F(p) is always closer to one than for the case where $n_{max} = 5$, and so on. The curve approaches the infinite case as more terms are added to the calculation. Numerically, the curves still asymptotically approach zero, and pseudo- p_{crit} remains at zero, even as more terms are added. The fact that the curves asymptotically approach zero, rather than the true p_{crit} , can cause problems when the solution algorithm uses the p_{crit} for some of the calculations. For example, the equations based on the infinite matrix are usually controlled by the value of p_{crit} . If the value of the p_{crit} is not equal to the apparent or pseudo- p_{crit} , then the equations may be incorrect for the infinite matrix.

With the implementation of the cut-off point technique, the only drawback is that the pseudo- p_{crit} is equal to zero. If the p_{crit} is not important in the problem, the cut-off technique works great. An approximate value of the pseudo- p_{crit} can be calculated if a small number, (such as 10^{-8}) is used to numerically approximate zero. For example, if a value of 10^{-4} (for the fraction of sites contained in the infinite matrix) were used as the threshold of when the infinite matrix is no longer present, and a cut-off point of 5 was used, the pseudo- p_{crit} would be 0.053. So therefore, the fraction of the sites that would be contained in the infinite matrix would be 10^{-4} at a p of 0.053. Figure 7.3 shows how the calculated pseudo- p_{crit} changes with different cut-off values and various approximate zeros for the case with σ +1=3.



Figure 7.3 Changes in the pseudo $-p_{crit}$ as a function of n_{max} for different numerical values used to approximate zero (s+1=3).

When $n_{max} = 8$, the results reach the statistical asymptote of 0.5 in the example (σ +1=3). Therefore, if the value of p_{crit} is needed, one solution is to calculate a pseudo- p_{crit} from an approximate zero. Including more terms into the calculation will increase the calculated pseudo- p_{crit} toward the actual value of p_{crit} . In this project, the threshold of when the infinite matrix is no longer present used was 10⁻⁸. With the cut-off point of 6, this gives a pseudo- p_{crit} of 0.016. The pseudo- p_{crit} was then used in the equations governing the infinite matrix during the modeling.

Population Balance Theory

One of the main benefits of the percolation lattice statistics is that only two parameters (fraction of intact bridges and coordination number) are needed to calculate the distribution of the oligomers, light molecules and the infinite matrix (for a closed system). The closed form solution is computed with no need for iteration, hence decreasing the computational time. But since the percolation lattice statistics are based on only two parameters, the flexibility is limited.

Percolation lattice statistics have successfully been applied to coal and biomass pyrolysis, char combustion, and polyurethane foam pyrolysis. In all previous applications, the lattice for the particle or computational cell of material was treated as a batch reactor, with no formal treatment of liquid or gas flow into or out of the computational domain. Ho wever, for an open system the oligomers generated in one cell that travel to neighboring cells may experience different temperatures and concentrations and may react very differently than the oligomers that remain in the original computational cell the entire time. A Lagrangian approach (where the transient conditions of each fragment are tracked) could be used to track the history of the various oligomers, but this would be very complicated and time consuming. One method to solve this problem is to use population balances on each of the oligomers considered in the calculations.

A population balance theory has been developed to allow for flow in and out of the computational cell while calculating the distribution of monomer, dimers, trimers, etc., without the need for a Lagrangian type calculation. This theory uses three parameters: (1) the current distribution of oligomers and infinite matrix; (2) the fractional change in bridges; and (3) the coordination number. In this section, the population balance theory that is used in conjunction with the percolation lattice statistics based on bridge breaking and forming will be presented.

During reactions, bridges can either (a) break due to thermal rupture or (b) form due to crosslinking or reattachment. These two processes are treated differently in the population balance theory, and hence are discussed in two sections namely, bridge breaking and bridge forming. A diagram of the different processes that can occur during bridge breakage or formation is shown below in Figure 7.4, and will be used in the discussion of the population balance theory.



Figure 7.4 Diagram of different process occuring during bridge formation and breakage.

Bridge Breaking

The bridge breaking section of the population balance theory is a combination of (a) modified percolation lattice statistics for the infinite matrix and (b) a separate model for the break down of the finite oligomers. The mathematics behind the processes A, B and C in Figure 7.4 will be discussed in this section. The percolation lattice statistics are similar to the statistics reviewed earlier, but then modified for the break down of the finite oligomers. The model of the breakdown of the finite oligomers was developed from statistical relationships between the finite oligomers. The equations were tested against various hand counting exercises and the percolation lattice statistics.

Finite Oligomers

The goal of this section was to develop an analytical expression to show how the distribution of a group of oligomers would change with a decrease in the number of bridges. This corresponds to Process A in Figure 7.4. The fractional decrease in bridges

(dp, e.g., a 10% decrease in the number of bridges gives a dp = 0.1) refers to only the decrease in the number of bridges due to reactions and not due to flow. The dp can be calculated from the bridge rate equations. For example, using the rate equations in Table 6.2, the fractional decrease in bridges is defined as:

$$dp = 1 - \frac{L_1^{(t-\Delta t)} + L_2^{(t-\Delta t)} + L_3^{(t-\Delta t)} + L_4^{(t-\Delta t)}}{L_1 + L_2 + L_3 + L_4}$$
(7.9)

where L_i is the population of bridge type i, calculated from the rate equations before the effects of flow have been considered for that time step, and $L_i^{(t-\Delta t)}$ is the previous population of bridge type i.

The primary assumptions for this theory are that the oligomers do not contain "loop" structures, are straight chain molecules and all the bridges have an equal reactivity. The stipulation that the oligomers are straight chains was necessary to simplify the problem. This stipulation does not affect the results of the polyurethane foam decomposition, since the only oligomers with significant amounts that left the computational cell were smaller than a 4 mer. The monomers, dimers and trimer are always straight chains and so the equations derived here are applicable. Only a small error would arise if larger branched oligomers were found to leave the computational cell. The modifications needed to take into account the larger branched oligomers are left to future researchers. The basic equation that describes the mole fraction of an n-sized oligomer (n-mer) that formed an m-sized oligomer (m-mer) is shown below:

$$\frac{mol_{n\to m}}{mol_n} = \sum_{br=0}^{n-1} C_{nmbr} (dp)^{br} (1-dp)^{n-1-br}$$
(7.10)

where

$$C_{nmbr} = \begin{cases} (br+1) \cdot \binom{n-m-1}{br-1} & m \le n-br, br \ge 1 \\ 0 & m > n-br, br \ge 1 \\ 1 & m = n, br \ge 0 \\ 0 & m \ne n, br = 0 \end{cases}$$
(7.11)

Here br is the number of bridges in the n-mer that where broken. The number of broken bridges in the n-mer (br) can range from 0 to n-1 (total bridges for an n-mer). The first term in Equation 7.10 (C_{nmbr}) is the number m-mers formed from an n-mer, based on the number of distinct ways to break br bridges in an n-mer. The second term is the probability that br bridges broke, while the third term is the probability that n-1-brbridges did not break. The n-1 term in the exponent of the third term comes from the fact that there are always n-1 bridges in an n-mer that does not contain any "loop" structures. Equation 7.10 has the same form as the binomial distribution, except the coefficient (C_{nmbr}) is different. The justification for the form of C_{nmbr} in Equation 7.11 can be found in Appendix C.

Tables 7.1 and 7.2 show the value of C_{nmbr} for a 5-mer and a 6-mer, respectively, for various values of br. For example when two bridges in the 5-mer are broken (i.e. br = 2), there are 6 distinct possibilities. Within these six possibilities, 9 monomers, 6 dimers, and 3 trimers are generated. There is no possible way to have either an oligomer greater than or equal to a 4-mer. As seen in the tables, the pattern of C_{nmbr} for the 5-mer is repeated in the C_{nmbr} for the 6-mer, only displaced down one row, showing the dependence of the C_{nmbr} versus n-m and br rather than simply n and br.

C_{nmbr}		br						
		0	1	2	3	4	5	6
m	1	0	2	9	12	5	0	0
	2	0	2	6	4	0	0	0
	3	0	2	3	0	0	0	0
	4	0	2	0	0	0	0	0
	5	1	0	0	0	0	0	0
	6	0	0	0	0	0	0	0
	7	0	0	0	0	0	0	0

Table 7.1C_{nmbr} for a 5-mer.

		Table	1.4	Unmbr	-nmbr 101 a 0-111cl.			
C_{nmbr}		br						
		0	1	2	3	4	5	6
	1	0	2	12	24	20	6	0
	2	0	2	9	12	5	0	0
m	3	0	2	6	4	0	0	0
	4	0	2	3	0	0	0	0
	5	0	2	0	0	0	0	0
	6	1	0	0	0	0	0	0
	7	0	0	0	0	0	0	0

Table 7.2C_{nmbr} for a 6-mer.

With Equations 7.10 and 7.11, the various oligomer sizes produced from process A (as shown in Figure 7.4) can be calculated. An example calculation is illustrated below. For a given system containing 0.2 moles each of monomers, dimers, trimers, 4-mers and 5-mers, the new distribution of the fragments with a 10% decrease in the bridges (dp = 0.1) can be calculated through Equations 7.10 and 7.11. Using the values for C_{nmbr} seen in Table 7.1, the amount of 5-mers that remain as 5-mers is then calculated as:

$$\frac{mol_{5\to 5}}{mol_5} = \sum_{br=0}^{4} C_{55br} (0.1)^{br} (0.9)^{4-br}$$

$$= 1 \cdot 0.1^{\circ} \cdot 0.9^{4} + 0 \cdot 0.1^{\circ} \cdot 0.9^{\circ} + 0 \cdot 0.1^{\circ} \cdot 0.9^{\circ}$$

= 0.6561 (7.12)

Therefore for a 10% decrease in the number of bridges, 65.61% of the 5-mers do not break down into smaller fragments, and 34.39% do breakdown into smaller fragments. Since the starting amount of 5-mer is 0.2 moles, then 0.1312 (0.6561 \times 0.2) moles of 5-mer remain as 5-mer. The number of moles of 4-mer generated from the 5-mers can be calculated by:

$$\frac{mol_{5\to4}}{mol_{5}} = \sum_{br=0}^{4} C_{54br} (0.1)^{br} (0.9)^{4-br}$$

= 0 \cdot 0.1⁰ \cdot 0.9⁴ + 2 \cdot 0.1¹ \cdot 0.9³ + 0 \cdot 0.1² \cdot 0.9² + 0 \cdot 0.1³ \cdot 0.9¹ + 0 \cdot 0.1⁴ \cdot 0.9⁰
= 0.1458 (7.13)

Since the starting amount of 5-mer is 0.2 moles, 0.0292 (0.1458 × 0.2) moles of 4-mer are generated from the 5-mers. Similarly the moles of monomer generated from the 5-mer can be calculated by:

$$\frac{mol_{5\to1}}{mol_{5}} = \sum_{br=0}^{4} C_{51br} (0.1)^{br} (0.9)^{4-br}$$

= 0 \cdot 0.1⁰ \cdot 0.9⁴ + 2 \cdot 0.1¹ \cdot 0.9³ + 9 \cdot 0.1² \cdot 0.9² + 12 \cdot 0.1³ \cdot 0.9¹ + 5 \cdot 0.1⁴ \cdot 0.9⁰
= 0.23 (7.14)

Since the starting amount of 5-mer is 0.2 moles, $0.046 (0.23 \times 0.2)$ moles of monomer are generated from the 5-mers. These results as well as the remaining terms are shown in Table 7.3. The numbers in the table represent the moles of the oligomer that were generated. For example, the 0.1620 term indicates that for a 10% decrease in the bridges, 0.1620 moles of trimers were generated from the 4-mer. The blank cells in Table 7.3

indicate the terms that are zero (i.e. generating larger oligomers from a smaller oligomer by breaking bridges).

n\m	1	2	3	4	5
1	0.2000				
2	0.0400	0.1800			
3	0.0420	0.0360	0.1620		
4	0.0440	0.0378	0.0324	0.1458	
5	0.0460	0.0396	0.0340	0.0292	0.1312
Total	0.3720	0.2934	0.2284	0.1750	0.1312

Table 7.3	Example calculations using the population balance theory bridg	ge
	breaking equations.	

* starting conditions: 0.2 moles each of monomers, dimers, trimers, 4mers and 5-mers

After summing all the term from the various oligomers, the new distribution shows that there are 0.3720, 0.2934, 0.2281, 0.1750 and 0.1312 moles of monomers, dimers, trimers, 4-mers and 5-mers, respectively. As seen in this example, the total number of moles increased as the bridges were breaking (0.372 + 0.2934 + 0.2281 + 0.175 + 0.1312 = 1.2, which is greater than the initial 1 mole). This is expected, since as you break large fragments into smaller fragments, the number of fragments increases. Although the number of moles increased, mass is conserved. Checking if the total moles of sites are the same as the initial distribution can show that the mass is conserved. In this example, it can be shown that the total moles of sites remained constant. Initially there were

$$1 \times 0.2 + 2 \times 0.2 + 3 \times 0.2 + 4 \times 0.2 + 5 \times 0.2 = 3$$

moles of sites, and after the bridge breaking there were

$$1 \times 0.372 + 2 \times 0.2934 + 3 \times 0.2281 + 4 \times 0.175 + 5 \times 0.1312 = 3$$

moles of sites. Furthermore, in this example it can be shown that the total moles of bridges decreased 10% (dp = 0.1). Initially there were

 $0 \times 0.2 + 1 \times 0.2 + 2 \times 0.2 + 3 \times 0.2 + 4 \times 0.2 = 2$

moles of bridges, and after the breaking of the bridges there were

 $0 \times 0.372 + 1 \times 0.2934 + 2 \times 0.2281 + 3 \times 0.175 + 4 \times 0.1312 = 1.8$

moles of bridges, which is 90% of the original moles of bridges.

Infinite Matrix

This section describes how the infinite matrix changes as the bridges are breaking, corresponding to processes B and C in Figure 7.4. Note that bridges can break and still leave the infinite matrix intact. One of the main assumptions of percolation lattice theory is that the breakup can be related to the initial matrix, and that all products (monomers, dimers, etc., as well as light molecules) originated from the infinite matrix. The fact that oligomers and light molecules can flow into or out of the cell complicates this treatment.

In this approach, a "phantom system" is used to accommodate the percolation lattice statistics, which always refers to the initial infinite matrix. Since some of the detached fragments may have been transported to a neighboring cell, the phantom system still permits the use of percolation lattice statistics. This phantom system is calculated from the initial infinite matrix and includes the finite oligomers and light molecules that are predicted from the percolation lattice statistics.

The need for the phantom system is illustrated by the following example. Suppose that the initial matrix reacts to form monomers, dimers and trimers. Due to flow of gas and liquid to neighboring cells, only 50% of these oligomers remain in the cell. At this time, the reaction scheme says that additional bridges are broken randomly between the infinite matrix and the oligomers, based on the initial configuration. Making additional oligomers from the infinite lattice is not a problem, but making dimers and monomers from the trimers and making monomers from the dimers is a big problem, since 50% have left the cell and may be at a different temperature. The phantom oligomer system is one convenient way to address this problem.

Knowing the mass of the infinite matrix and the fraction of intact bridges in the infinite matrix, the mass of the initial infinite matrix can be calculated, which is equal to the mass of the phantom system. With the mass of the phantom system, the mass of each oligomer being considered in the phantom system can be calculated from percolation lattice statistics.

Next, the change in the mass of the finite oligomers and the infinite matrix is calculated from the percolation lattice statistics, based on the kinetic rates from the chemical mechanism. The percolation lattice statistics can be thought off as a combination of processes A, B and C (see Figure 7.4). Since a solution for process A has been developed (see Finite Oligomers section), this solution can be subtracted from the percolation lattice statistics to get a solution for processes B and C. This is illustrated in the following example. Suppose the phantom system contains some phantom 4 mers with the current infinite matrix. The 4-mers have actually been transported to a neighboring cell. The percolation lattice statistics will calculate that along with trimers, dimers, and monomers being formed from the break down of the infinite matrix (process B), some of these n-mers would be formed from the breakdown of the phantom 4-mers as well (process A). To account for this, the amount of trimers, dimers, and monomers that would have been formed by the phantom 4-mers can be calculated using Equations 7.9 and 7.10 as discussed above. The resulting amounts of trimers, dimers and monomers are

then subtracted from the calculated mass generation from the breakdown of the phantom system (processes A, B and C) to correctly obtain the mass generation from the breakdown of the infinite matrix alone (processes B and C). The calculated oligomer mass generated reduces the mass of the infinite matrix (process C). Once the p reaches the p_{crit} , the infinite matrix calculations (processes B and C) should no longer be performed. The phantom system therefore represents the calculation of a hypothetical closed system, and serves as a convenient device to still use the percolation lattice statistics when some oligomers have left the computation cell.

Bridge Forming

This section describes the statistical relationships of forming bridges between the detached fragments and the infinite matrix (processes D, E and F, Figure 7.4). The major assumptions regarding bridge formation is that no "loop" structures are formed and that each side chain that is reacting to form a bridge has an equal reactivity. This theory is also broken into two sections, one for forming finite oligomers (process D), and the other for attaching to or cross-linking within the infinite matrix (processes E and F). The model for the finite oligomers is based on the statistical relationships of forming bridges between reactive groups. The treatment of the infinite matrix is mainly based on a mass and mole balance of the different components of the infinite matrix.

Finite Oligomers

The bridge forming portion of the population balance theory is much more complex than the bridge breaking section. For example, a monomer that formed only one new bridge could connect with another monomer (process D) or a 7-mer (process D) or reattach back to the infinite matrix (process E). The monomer that connected with another monomer to form dimer, could have stopped reacting and then remained a dimer (see 2-group in Figure 7.5 below). However, this newly formed dimer could have simultaneously connected with another monomer (process D), or a 7-mer (process D) or reattach back to the infinite matrix (process E). The three monomers that connected together to form a trimer, could have stopped reacting and then remained as a trimer (see 3-group in Figure 7.5 below). However, this newly formed trimer could have simultaneously connected with other fragments and so forth. This process can continue on and on, and must be simplified to create a manageable solution. The approach used to describe formation of bridges from oligomers is discussed as follows: (a) the simplifying approaches are discussed first; (b) the mathematical solution to calculate the amount of oligomers formed is derived; (c) further simplifications derived from the mathematical solutions are reviewed; and finally, (d) a numerical example of the calculations using the derived equations.

Simplifying Approaches

One method to simplify the bridge forming relations is to categorize the different possibilities by the total number of oligomers that were reattached and the manner that they were connected. A picture of the smallest seven categories is shown below in Figure 7.5 (without forming any "loop" structures). A circle represents each oligomer, while the solid line represents the bridge formed between them. The oligomers are labeled with letters from i to m for reference in future equations. The oligomers were labeled from the most connected oligomer (i.e. i denotes the greatest number of bridges formed), and then from left to right if the number of bridges formed is the same for two oligomers.



Figure 7.5 Representation of the seven smallest groups of oligomer reattachments. (Here i, j, k, l, and m represent oligomers)

There is only one way to connect two oligomers, while on the other hand, there are three ways to connect five oligomers (without forming any "loop" structures). In the case of two oligomers connecting together (2-group, see Figure 7.5), each oligomer formes only one bridge. One oligomer forms two bridges, while the other two oligomers each form one bridge in the case of three oligomers connecting together (3-group, see

Figure 7.5). Two situations occur in the case of four oligomers connecting together (4aand 4b-groups, see Figure 7.5): a) two oligomers form two bridges and two oligomers form one bridge; and b) one oligomer forms three bridges and three oligomers form one bridge. Three situations occur in the case of five oligomers connecting together (5a-, 5band 5c-groups, see Figure 7.5): a) three oligomers form two bridges and two oligomers form one bridge; b) one oligomer forms three bridges, one oligomer forms two bridges, and three oligomers form one bridge; and c) one oligomer forms four bridges and four oligomers form one bridge.

The next simplifying approach is to use the cut-off point technique. If only n_{max} oligomer groups are being tracked in the calculation, then every oligomer generated that has a size greater than n_{max} is lumped into the infinite matrix. The different configurations considered in each group are therefore reduced further. To illustrate, for a monomer in the 2-group with n_{max} =10, the maximum oligomer size that will be considered for reattachment is a 9-mer, while for a 5-mer it is a 5-mer. Now in the 5a-group, for a 1-mer-2-mer-3-mer-1-mer-?-mer, the final piece must be less than or equal to a 3-mer. As seen in these examples, as the total number of oligomer sizes that are tracked decreases (i.e., as n_{max} decreases), the number of possibilities in each group decreases.

Mathematical Solution

With these simplifying approaches in mind, the mathematical representation of the oligomer reattachment can be discussed. First, the fractional decrease in the number of side chains (dsc) that came from the conversion of side chains to bridges only, and

not any reactions of side chains to something else, needs to be calculated. This is much easier when the bridge reactions are structured such that side chains are only generated from bridges or other side chains. In this case, the number of side chains is only changed by the reactions of side chains to bridges, since if a side chain reacts to form a different side chain, the number of side chains did not change. The equation for the fractional decrease in the number of side chains can then be written in terms of the bridge populations defined in Table 6.2:

$$dsc = \frac{2 \cdot \left[\left(L_1 + L_2 + L_3 + L_4 \right) - \left(L_1^{(t-\Delta t)} + L_2^{(t-\Delta t)} + L_3^{(t-\Delta t)} + L_4^{(t-\Delta t)} \right) \right]}{D_1 + D_2 + D_3 + D_4 + D_5 + D_6}$$
(7.15)

where L_i is the population of bridge type i, calculated from the rate equations before the effects of flow have been considered for that time step, $L_i^{(t-\Delta t)}$ is the previous population of bridge type i, and D_i is the population of side chain type i, calculated from the rate equations before the effects of flow have been considered for that time step.

Next, the number of side chains on an oligomer (t_n) must be evaluated. This is calculated, as discussed earlier in Equation 2.15, by:

$$\boldsymbol{t}_n = [n(\boldsymbol{s}-1)+2] \tag{7.16}$$

Once the number of side chains (t_n) for the n-mer is known, the mole fraction of newly formed bridges for each oligomer can be calculated. Instead of just calculating a single number of side chains that formed bridges, a distribution must be used to adequately model the system. For example, a system of twenty monomers (σ +1=3), with 10% of the side chains reacting to form bridges, is shown below in Figure 7.6. The reacted side chains are circled in the figure.



Figure 7.6 Representation of twenty monomers with 10% of the side chains reacted randomly to form bridges. (s+1=3) (The circled side chains represent reacted side chains)

As seen in Figure 7.6, for this case, 75% of the monomers did not form bridges, 20% of the monomers formed one bridge, 5% of the monomers formed two bridges, and none of the monomers formed three bridges. If this case is repeated several billion times randomly distributing the side chains that reacted to form bridges, the true distribution can be found.

An equation for the mole fraction of an n-mer that formed fr bridges as a function of dsc (fraction of side chains that reacted) can be derived from the binomial distribution. The variable fr is used in the computational loop in the calculations. The standard binomial distribution form can be applied since there are only two possible outcomes for each side chain, forming a bridge or not. The equation used to calculate the distribution of how many bridges an oligomer formed on a mole fraction basis is:

$$\frac{mol_n^{fr}}{mol_n} = {\binom{t_n}{fr}} \cdot (1 - dsc)^{t_n - fr} \cdot dsc^{fr}$$
(7.17)

This equation has essentially the same form as Equation 2.14 in the percolation lattice statistics and Equation 7.10 in the bridge breaking section of the population balance

theory. Applying Equation 7.17 to the example shown in Figure 7.6, the true distribution (of 72.9%, 24.3%, 2.7% and 0.1%, for the mole fraction of monomers that formed 0, 1, 2, and 3 bridges, respectively,) can be calculated. A bar graph of the distribution of the formed bridges for a monomer, dimer, trimer, 4-mer, 10-mer and 20-mer is shown below in Figure 7.7. In this calculation σ +1 = 3, and *dsc* = 0.10. As seen in Figure 7.7, as the oligomer size increases, the distribution shifts to the right (i.e., the mole fraction of oligomer that formed bridges increases). This is due to the fact that as the oligomer size increases, the number of side chains increase.



Figure 7.7 Distribution of reacted side chains as a function of oligomer size (s+1=3, 10%) of side chain formed bridges)

With more side chains, there is a higher probability that one or more of the side chains reacted to form a bridge. For a monomer with three side chains (σ +1=3), if 10%

of the side chains react, it is most likely that 0.3 side chains reacted. Since a fractional fr does not make sense, a value of fr = 0 ends up being the most likely. However, for a 10-mer with 12 side chains, if 10% of the side chains react, it is most likely that 1.2 side chains reacted, which gives the highest percent to the fr = 1 column. Likewise for a 20-mer with 22 side chains, this gives 2.2 reacted side chains as being the most likely situation and the highest percent in the fr = 2 column as seen in Figure 7.7.

Once the quantities of side chains that form bridges are calculated, as outlined above and illustrated in Figure 7.7, the population of each oligomer size must be recalculated in a consistent manner. For example, if a monomer attaches to a dimer, the population of monomers and dimers must be decreased and the population of trimers must be increased. The easiest configuration to consider as an example is the 2-group from Figure 7.5. The 2-group represents an i-mer that formed only one connection and connected with a j-mer with only one connection. An equation to calculate the number of moles of an (i+j)-mer generated (mol_{i+j}^{gen}) can be derived from the following procedure. First, the total moles of i-mer (mol_i) , at the beginning of the time step, should be multiplied by the mole fraction of the i-mers that only formed one bridge $(\frac{mol_i}{mol_i})$, which

comes from Equation 7.17. Then that product should be multiplied by the probability that the i-mer reacted with a j-mer that only formed one bridge $(prob_j^1)$. This is illustrated below in Equation 7.18:

$$mol_{i+j}^{gen} = mol_i \cdot \frac{mol_i^1}{mol_i} \cdot \frac{prob_j^1}{2}$$
(7.18)

The factor of two in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-3 is different than the set 3-1).

The probability $(prob_j^1)$ is defined as the ratio of the number of reacted side chains on the j-mer (tot_j^{fr}) to the total number of reacted side chains (tot_j^{fr}) :

$$prob_n^{fr} = \frac{tot_n^{fr}}{tot^{fr}}$$
(7.19)

The total number of reacted side chains on an n-mer with fr reacted side chains is simply fr multiplied by the moles of n-mer (mol_n) , and then multiplied by the mole fraction of the n-mer with fr reacted side chains (Equation 7.17), and is shown below in Equation 7.20.

$$tot_n^{fr} = \begin{pmatrix} \mathbf{t}_n \\ fr \end{pmatrix} \cdot (1 - dsc)^{\mathbf{t}_n - fr} \cdot dsc^{fr} \cdot fr \cdot mol_n$$
(7.20)

The total number of side chains that reacted can be calculated by summing the moles of side chains attached to the oligomers and the moles of side chains attached to the infinite matrix (sch_{inf}):

$$tot^{fr} = \left(\sum_{n=1}^{n \max} \boldsymbol{t}_n \cdot mol_n + sch_{\inf}\right) \cdot dsc$$
(7.21)

which is the same as calculating the total number of side chains and then multiplying by the percent decrease of side chains. Substituting Equations 7.17, 7.19-7.21 into Equation 7.18 and combining terms gives the equation for the mole generation of a (i+j)-mer (process D in Figure 7.4) for 2-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j}^{gen} = \frac{1 \cdot \begin{pmatrix} \boldsymbol{t}_{j} \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_{j} \\ 1 \end{pmatrix} \cdot (1 - dsc)^{\boldsymbol{t}_{i} + \boldsymbol{t}_{j} - 2} \cdot dsc^{2} \cdot mol_{i} \cdot mol_{j}}{2 \cdot tot^{fr}}$$
(7.22)

Now, when calculating the mole generation of a (i+j)-mer, there are n_{max}^{2} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 2-3 is a mirror image of 3-2). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max}) -mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-1, 2-2, etc.) These terms do not have a mirror image term, and so the factor of two in the denominator in Equation 7.19 and 7.22 should remain.

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner to the 3-, 4a-, 4b-, 5a-, 5b- and 5c-groups, respectively. The following equations are derived in Appendix D:

$$mol_{i+j+k}^{gen} = \frac{2 \cdot \begin{pmatrix} \boldsymbol{t}_{i} \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_{j} \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_{k} \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijk-4} \cdot dsc^{4} \cdot mol_{i-k}}{2 \cdot (tot^{fr})^{2}}$$
(7.23)

$$mol_{i+j+k+l}^{gen} = \frac{4 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijkl-6} \cdot dsc^6 \cdot mol_{i-l}}{4 \cdot (tot^{fr})^3}$$
(7.24)

$$mol_{i+j+k+l}^{gen} = \frac{3 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 3 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijkl-6} \cdot dsc^6 \cdot mol_{i-l}}{6 \cdot (tot^{fr})^3}$$
(7.25)

$$mol_{i+j+k+l+m}^{gen} = \frac{8 \cdot \binom{\boldsymbol{t}_i}{2} \cdot \binom{\boldsymbol{t}_j}{2} \cdot \binom{\boldsymbol{t}_k}{2} \cdot \binom{\boldsymbol{t}_l}{1} \cdot \binom{\boldsymbol{t}_m}{1} \cdot (1 - dsc)^{tijklm-8} \cdot dsc^8 \cdot mol_{i-m}}{12 \cdot (tot^{fr})^4}$$
(7.26)

$$mol_{i+j+k+l+m}^{gen} = \frac{6 \cdot \binom{\boldsymbol{t}_i}{3} \cdot \binom{\boldsymbol{t}_j}{2} \cdot \binom{\boldsymbol{t}_k}{1} \cdot \binom{\boldsymbol{t}_l}{1} \cdot \binom{\boldsymbol{t}_l}{1} \cdot (1 - dsc)^{tijklm-8} \cdot dsc^8 \cdot mol_{i-m}}{6 \cdot (tot^{fr})^4}$$
(7.27)

$$mol_{i+j+k+l+m}^{gen} = \frac{4 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 4 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_m \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijklm-8} \cdot dsc^8 \cdot mol_{i-m}}{24 \cdot (tot^{fr})^4}$$
(7.28)

where

$$tijk = t_i + t_j + t_k \tag{7.29}$$

$$mol_{i-k} = mol_i \cdot mol_i \cdot mol_k$$

$$\tag{7.30}$$

$$tijkl = t_i + t_j + t_k + t_l$$
(7.31)

$$mol_{i-l} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l$$
(7.32)

$$tijklm = t_i + t_j + t_k + t_l + t_m$$
(7.33)

$$mol_{i-m} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l \cdot mol_m$$
(7.34)

where the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5.

Further Simplifications

Further simplification can be made by mathematical approximations. As seen in Equations 7.22-7.28, as the number of oligomers that are considered in the group increases the exponents increase for the terms dsc, (1-dsc) and tot^{fr} . Since dsc and
(1-dsc) are always between zero and one, as their exponents increase, the magnitude of the term decreases. Since, tot^{fr} is always greater than or equal to mol_i , the ratio of the multiplication of the mol_i to the tot^{fr} will always be less than one, and so as the exponents increase, the magnitude of the term decreases further. The 2-group, or the 3-group terms may be the only significant terms for process D, depending on the conditions. Only the 2-group term will be significant as dsc approaches a differential value.

Numerical Example

To illustrate how the bridge forming equations work together to calculate the new distribution of the finite fragments, a numerical example is shown below. For a given system containing 0.2 moles each of monomers, dimers, trimers, 4-mers and 5-mers, the new distribution of the fragments with a 10% decrease in the side chains (dsc = 0.1) can be calculated using Equations 7.17 and 7.22-7.34. For this example a coordination number of four (σ +1 = 4) will be used. First, Equation 7.17 must be used to calculate the moles of the oligomers that did not react and hence did not form any bridges. An example calculation for the 5-mer is shown below. The number of side chains on a 5-mer (t_5) is required in Equation 7.17. With a coordination number of four (σ +1 = 4) t_5 is equal to twelve (Equation 7.16, $t_5 = 5 \cdot (3-1) + 2 = 12$). Therefore, Equation 7.17 becomes:

$$\frac{mol_5^0}{mol_5} = \begin{pmatrix} 12\\0 \end{pmatrix} \cdot (0.9)^{12} \cdot (0.1)^0 = 1.0 \cdot 0.2824 \cdot 1.0 = 0.2824$$
(7.35)

As seen in Equation 7.35, only 28.24% of the 5-mers did not form any bridges, therefore, $0.0565 (0.2 \times 0.2824)$ moles of 5-mer remain unaffected. The fraction of the other oligomers that did not form any bridges must also calculated in a similar manner.

Next, the moles of 5-mer that have been generated from two oligomers connecting together (i.e., the 2-group) can be calculated. First, the total number of reacted side chains (*tot*^{*fr*}) must be calculated (Equation 7.20), and is shown below. The number of side chains for a monomer (t_1), dimer (t_2), trimer (t_3), 4-mer (t_4) and 5-mer (t_5) with a coordination number of four (σ +1 = 4) are 4, 6, 8, 10 and 12, respectively (from Equation 7.15). Therefore, the total number of reacted side chains (*tot*^{*fr*}) is calculated from Equation 7.20:

$$tot^{fr} = (4 \cdot 0.2 + 6 \cdot 0.2 + 8 \cdot 0.2 + 10 \cdot 0.2 + 12 \cdot 0.2 + 0) \cdot 0.1 = 0.8$$
(7.36)

In this example, there are no side chains in the infinite matrix (i.e., $sch_{inf} = 0$).

There are two possibilities that would form a 5-mer, either a monomer connected to a 4-mer (1-4), or a dimer connected to a trimer (2-3). The calculation of the moles of 5-mer generated from a dimer and a trimer is found by using Equation 7.22:

$$mol_{5}^{gen} = \frac{1 \cdot \binom{6}{1} \cdot \binom{8}{1} \cdot (0.9)^{12} \cdot (0.1)^{2} \cdot 0.2 \cdot 0.2}{2 \cdot 0.8} = 0.0034$$
(7.37)

As seen in Equation 7.37, 0.0034 moles of 5-mer were generated from a dimer and a trimer connecting together. Now the calculation of a trimer connecting to a dimer would yield the same result. Consequently, the result is multiplied by two to account for this other possibility. Similarly, the calculation of the moles of 5-mer generated from a monomer and a 4-mer connecting to make a 5-mer is:

$$mol_{5}^{gen} = \frac{1 \cdot \binom{4}{1} \cdot \binom{10}{1} \cdot (0.9)^{12} \cdot (0.1)^{2} \cdot 0.2 \cdot 0.2}{2 \cdot 0.8} = 0.0028$$
(7.38)

As seen in Equation 7.38, 0.0028 moles of 5-mer were generated from a monomer and a 4-mer connecting together. Again, the calculation of a 4-mer connecting to a monomer would yield the same result. Consequently, the result is multiplied by two to account for this other possibility. This procedure (illustrated above for the 5-mer) is then repeated for the other oligomer sizes.

Next, the moles of 5-mer that were formed from three oligomers connecting (3group) can be calculated. There are two possibilities that would form a 5-mer, either, a monomer connected with another monomer, and connected with a trimer (1-1-3), or a monomer connected with two dimers (1-2-2). For each of these two possibilities, there are two different ways they can connect. In the first scenario, either the monomer (1-1-3) or the trimer formed two bridges (1-3-1), while in the second scenario, either the monomer (2-1-2) or the dimer (1-2-2) formed two bridges. The difference in the two cases is illustrated below. The calculations for the above scenarios are shown in Table 7.4. The calculation of 3-1-1 would yield the same results as seen for 1-1-3 in Equation 7.39, and the calculation of 2-2-1 would yield the same results as seen for 1-2-2 in Equation 7.41. Consequently, the results from these equations can be multiplied by two to account for these other possibilities, instead of recalculating the other terms. As seen in the results of the above equations, the mole generation terms from three oligomers connecting together to form a 5-mer are an order of magnitude small than the mole generation terms from the 2-group. The terms for the 4a-, 4b-, 5a-, 5b- and 5c-groups are even smaller, and hence are not shown.

Table 7.43-group calculations for a 5-mer.		
Scenario	Equation	Equation #
1-1-3	$mol_{5}^{gen} = \frac{2 \cdot \binom{4}{2} \cdot \binom{4}{1} \cdot \binom{8}{1} \cdot (0.9)^{10} \cdot (0.1)^{4} \cdot 0.2 \cdot 0.2 \cdot 0.2}{2 \cdot (0.8)^{2}} = 0.0001$	(7.39)
1-3-1	$mol_{5}^{gen} = \frac{2 \cdot \binom{8}{2} \cdot \binom{4}{1} \cdot \binom{4}{1} \cdot (0.9)^{10} \cdot (0.1)^{4} \cdot 0.2 \cdot 0.2 \cdot 0.2}{2 \cdot (0.8)^{2}} = 0.0002$	(7.40)
1-2-2	$mol_{5}^{gen} = \frac{2 \cdot \binom{6}{2} \cdot \binom{6}{1} \cdot \binom{4}{1} \cdot (0.9)^{10} \cdot (0.1)^{4} \cdot 0.2 \cdot 0.2 \cdot 0.2}{2 \cdot (0.8)^{2}} = 0.0001$	(7.41)
2-1-2	$mol_{5}^{gen} = \frac{2 \cdot \binom{4}{2} \cdot \binom{6}{1} \cdot \binom{6}{1} \cdot (0.9)^{10} \cdot (0.1)^{4} \cdot 0.2 \cdot 0.2 \cdot 0.2}{2 \cdot (0.8)^{2}} = 0.0001$	(7.42)

A summary of the above example for the 5-mer, along with the results of additional calculation for the smaller oligomers, is shown in Table 7.5. The terms that are multiplied by two in Table 7.5 came from oligomer combinations that had mirror image conformations (e.g., 1-3 and 3-1; 2-2-1 and 1-2-2; etc.) The individual mole generation terms used in the calculations are separated in the table to allow for a better understanding.

Table 7.5Example calculations using the population balance theory bridge
forming equations

n	Unreacted	2 group	3 group	Total
1	0.1312	0.0	0.0	0.1312
2	0.1063	0.0021	0.0	0.1084
3	0.0861	$2 \times 0.0026 = 0.0052$	0.0001	0.0914
4	0.0697	$2 \times 0.0028 + 0.0031 = 0.0087$	$2 \times 0.0006 + 0.0005 = 0.0017$	0.0801
5	5 0.0565	2×0.0028 + 2×0.0034 =	2×0.0001+ 0.0002	0.0606
3		0.0124	$2 \times 0.0001 + 0.0001 = 0.0017$	0.0090

As seen in Table 7.5, the distribution of the finite fragments changed from 0.2, 0.2, 0.2, 0.2 and 0.2 to 0.1312, 0.1084, 0.0914, 0.0801 and 0.0696 for the monomers, dimers, trimers, 4-mers and 5-mers, respectively, for a 10% decrease in the number of side chains (i.e., dsc = 0.1). The remaining sites, bridges and side chains are then assumed to be associated with the infinite matrix for this calculation, and is discussed in further detail below.

Infinite Matrix

The treatment of the infinite matrix is based on a mass balance, along with a mole balance of the different structures. The total number of sites, bridges and side chains being considered in the calculation of the finite oligomers (process D) is calculated on a mole basis. Since there are many structures that are assumed to be large enough to be considered as part of the infinite matrix, calculating each structure and then summing them together would require a lot of computational time. Instead, after the masses of the oligomers are calculated from Equations 7.17 and 7.22-7.28, as illustrated in the example summarized in Table 7.5, it is assumed that the rest of the mass must be part of the infinite matrix (processes E and F). If some of the terms that are being ignored are important, then the oligomers that would have been calculated are now incorporated into the infinite matrix (process E), increasing the mass of the infinite matrix. For example, consider the case where the terms from the 1-mer-1-mer-1mer-1-mer calculated from Equations 7.26-7.28 totaled 1 mg. If these terms were ignored, then the calculated mass of the 5-mers would be 1 mg lower than it should be and the calculated mass of the infinite matrix would be1 mg higher than it should be. Now on the other hand, for the case where the terms from the 1-mer-1-mer-1mer-1-mer calculated from Equations

7.26-7.28 totaled 1 μ g, and the total mass in consideration was 50 mg, the exclusion of these terms would not be very noticeable. These factors should be considered when deciding how many terms to include in the calculations. In general, the 4- and 5-group terms are not significant in most calculations.

Continuing the numerical example from above, the distribution of the finite fragments changed from 0.2, 0.2, 0.2, 0.2 and 0.2 to 0.1312, 0.1084, 0.0914, 0.0801 and 0.0696 for the monomers, dimers, trimers, 4 mers and 5 mers, respectively, for a 10% decrease in the number of side chains (i.e., dsc = 0.1). Other larger oligomers were also generated during the bridge formation. These larger oligomers are all associated with the infinite matrix. The properties of the infinite matrix can then be calculated from a mole balance of the sites and bridges. The initial moles of sites were

 $1 \times 0.2 + 2 \times 0.2 + 3 \times 0.2 + 4 \times 0.2 + 5 \times 0.2 = 3$

moles, and after the bridge formation the moles of site contained in the oligomers were

$$1 \times 0.1312 + 2 \times 0.1084 + 3 \times 0.0914 + 4 \times 0.0801 + 5 \times 0.0696 = 1.2906$$

moles of sites. This means that 1.7094 (3.0 - 1.2906) moles of sites are contained in the infinite matrix. Furthermore, the initial moles of side chains were

 $4 \times 0.2 + 6 \times 0.2 + 8 \times 0.2 + 10 \times 0.2 + 12 \times 0.2 = 8$

moles, and after the bridge formation there were

$$4 \times 0.1312 + 6 \times 0.1084 + 8 \times 0.0914 + 10 \times 0.0801 + 12 \times 0.0696 = 3.5426$$

moles of side chains. The total moles of side chains should be 7.2 (8×0.9). This means that 3.6574 (7.2 – 3.5426) moles of side chains are contained in the infinite matrix. For 1.7094 moles of sited in the infinite matrix there should be 3.4188 moles of bridges and side chain divided by two (see percolation lattice statistics). This means that there would

be 1.5901 (3.4188 - 3.6574 / 2) moles of bridges in the infinite matrix. The initial moles of bridges were

$$0 \times 0.2 + 1 \times 0.2 + 2 \times 0.2 + 3 \times 0.2 + 4 \times 0.2 = 2$$

moles, and after the bridge formation there were

$$0 \times 0.1312 + 1 \times 0.1084 + 2 \times 0.0914 + 3 \times 0.0801 + 4 \times 0.0696 + 1.5901 = 2.4$$

moles. The total moles of bridges increased by 120%, which is expected during bridge formation. Using Equation 7.15 gives:

$$dsc = \frac{2 \cdot (2.4 - 2.0)}{8} = \frac{2 \cdot 0.4}{8} = \frac{0.8}{8} = 0.1$$
(7.42)

which was the predetermined value.

Evaluation

To evaluate the above models, several test cases were used. Each section of the model was tested separately and was checked to insure that the solution would give the same answer as the percolation lattice statistics if no flow were involved. The percolation lattice statistics have a closed form solution for a closed system that has been shown to match very well with actual lattice break down (Fisher and Essam, 1961). The population balance equations were developed in this project and need to be evaluated versus a reliable comparison.

Bridge Breaking

The first test case for the bridge breaking model was the breakdown of an infinite matrix without any flow in or out of the cell. The results were compared with the percolation lattice statistics for various decreases in the bridge population. The relative difference between the two models was very low and similar to the numerical precision of the machine (10^{-16}) for all the cases tested. The results were compared with how many intermediate steps were taken to reach the end. The number of intermediate steps was varied from one to 10,000. As the number of intermediate steps increased, the relative difference between the two models increased to ~ 10^{-14} for 10,000 steps. The source of this error is more likely a result of the numerical round-off due to the significant digits stored in the memory of the computer, which was then compounded with every time step.

The next test cases for the bridge breaking model were to examine the effect when flow out was introduced. For these cases, it was assumed that all of the monomers, or the monomers and dimers, etc., were carried out of the computational cell by the flow. The main check was to determine if any of the masses calculated were less than zero, or if there was a difference in the masses of the higher sized oligomers. The model passed both criteria for the several test cases. Again, the relative error increased slightly to 10^{-14} when the number of intermediate steps was increased to 10,000.

Bridge Forming

The first test cases for the bridge forming section were to start with a system at a p of 0.1, and then form bridges until the p reached 0.5, with no flow in or out of the cell. The masses of the oligomers were compared with the masses calculated by the percolation lattice statistics. Since in this section some of the terms were ignored, the relative error for the oligomers was generally higher than the machine precision. A comparison of the relative error versus the number of intermediate step and versus the

groups that were added in the calculations was made and can be seen below in Figures 7.8 for monomers reattaching and in Figure 7.9 for a 5-mer reattaching. Calculations were performed for the 2-, 3- and 4-groups as shown in Figure 7.5.



Figure 7.8 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the monomers. (Bridge forming, s+1=3)

As seen in Figure 7.8, the relative error generally decreased as the number of intermediate steps increased. For the 2-, 3-group and the 2-, 3-, 4-group, the relative error increased as the number of intermediate steps increased after 10,000 intermediate steps. This is most likely caused by the increase in the numerical error from the round off of the computer.

As seen in Figure 7.9, the decrease in the relative error was fairly linear for the 5mer sizes, except when the relative error approaches 10^{-8} - 10^{-12} and the error levels off and then increases with increased steps. The relative error for the other oligomer sizes was also measured and showed similar results (see Appendix E).



The rate of decrease of the relative error for the calculations with only the 2-group is approximately half the rate of decrease for the calculations with the 2-, 3-groups and the 2-, 3-, 4-groups. For the 2-group, as the number of intermediate steps increased an order of magnitude, the relative error decreased an order of magnitude. For the 2-, 3- groups and the 2-, 3-, 4-groups, as the number of intermediate steps increased an order of magnitude, the relative error decreased two orders of magnitude. This would correspond to a rate of convergence of n for the 2- group, and n^2 for the 2-, 3-groups and the 2-, 3-, 4- groups. Interestingly, the rate of convergence did not significantly increase when the 4-

group terms were added to the calculation. The relative error decreased almost an order of magnitude, but the rate of decrease did not change.

As the number of intermediate steps increased to 1,000,000, the relative error of all the oligomers approached a value of 10^{-10} for the 2-, 3-groups and the 2-, 3-, 4-groups. This is most likely caused by the increase in the numerical error from the round off of the computer. Other test cases used involved increasing the p to a value of 0.3 and 0.7 were also used and similar results were obtained, showing that the end point of the test case did not affect the results (see Appendix E)

Next the bridge forming theory was tested with flow conditions in and out of the cell to check for negative mass calculations, and if the masses of the oligomers were above or below the calculated values from the percolation lattices statistics according to the situation. The calculations did not produce any negative masses (a common byproduct of other methods used in correcting for flow), and matched the expected distributions.

Both the bridges breaking and bridge forming sections of the theory showed very good agreement with the percolation lattice theory. The bridge breaking calculations agreed within the machine precision for all the cases tested. From the test cases, it appeared that the inclusion of the 2- and 3-groups into the bridge forming calculations increased the accuracy of the prediction, while adding the 4-group did not increase the accuracy of the prediction enough to account for the increase in computational time. Therefore it is recommended that for the bridge forming theory, the 2- and 3-groups be used in the calculations. The number of intermediate steps dictates the desired level of

accuracy. The population balance theory equations are great tools for determining the distribution of the oligomers from the bridge and side chain reactions.

Chapter 8. Flow and Phase Characteristics

The approach to modeling the confinement or flow characteristics is discussed first in this chapter. The calculation of the inlet flow masses of each species is reviewed next. The vapor/liquid/solid equilibrium is presented, along with a discussion of the compressibility of the gas. The determination of the outlet flow masses of each species is then outlined. Finally, the conversion of the inlet and outlet flow masses to a population basis is presented.

Flow Approach

The effects of confinement are considered for a single control volume, which would correspond to a cell in a CFD calculation. The control volume is treated as containing a mass of gas (M_g) and condensed phase (M_c) , which are then mixed together with a mass of inlet flow gas (M_g^{in}) and condensed phase (M_c^{in}) in the general case. After vaporization, the control volume contains an adjusted mass of gas (M_g^{a}) and condensed phase (M_c^{out}) and condensed phase (M_c^{out}) and condensed phase (M_c^{out}) and condensed phase (M_c^{out}) leaves the system according to the applied forces (pressure, gravity, etc.) This is represented below graphically in Figure 8.1, where the double line shows the boundaries of the control volume.



Figure 8.1 Graphical representation of the mixing of the control volume with an inlet flow, to produce the modified control volume, and an outlet flow.

Inlet Flow Mass

For the unconfined case, the mass of the inlet flow gas is calculated from given conditions of the experiment, and there is no inlet flow of a condensed phase. For the partially- and totally-confined cases, there is no inlet flow of either a gas phase or condensed phase. For the general case, there is both an inlet flow of a gas and condensed phase, which are calculated from the surrounding cell conditions.

The inlet flow mass and the current mass of each species are added together and the moles of each species are then calculated by dividing by the molecular weight of the species. The total number of moles is then used to calculate the mole fraction of each species for use in the vapor/liquid/solid equilibrium submodel.

Vapor/Liquid/Solid Equilibrium

With the molecular weights and mole fractions of the n-mers and the light molecules, the calculation of the overall fraction that vaporized and the calculation of the outlet flow and remaining mass (taking into account the amount of confinement) can be made. The fraction of the species that are in the gas and condensed phase can be determined by using a simple vapor-liquid equilibrium relationship applying Raoult's law. A standard multi-component isothermal flash calculation is used with the Rachford-Rice equation (Seader and Henley, 1998) to determine the split of the total moles between vapor and condensed phase by solving the following equation for V/F:

$$0 = \sum_{i=1}^{n} \frac{z_i (K_i - 1)}{(K_i - 1) \frac{V}{F} + 1}$$
(8.1)

where

$$K_i = \frac{y_i}{x_i} = \frac{P^*}{P} \tag{8.2}$$

V/F is determined iteratively from Equation 8.1. The parameters z_i , x_i , and y_i represent mole fractions in the overall, condensed phase, and vapor phase, respectively. V and F represent the total moles in the vapor phase and overall, respectively. P^* represents the vapor pressure of the pure component at the system temperature. The mole fractions in the condensed and vapor phases can be determined as follows:

$$x_{i} = \frac{z_{i}}{(K_{i} - 1)\frac{V}{F} + 1}$$
(8.3)

and

$$y_{i} = \frac{K_{i}z_{i}}{(K_{i} - 1)\frac{V}{F} + 1}$$
(8.4)

The "K-values" defined in Equation 8.2 can be determined from the vapor pressure of the pure components, P^* , divided by the system pressure. For the n-mers, the vapor pressure is determined through a correlation known as the Fletcher-Grant-

Pugmire (FGP) correlation (Fletcher et al., 1992a; 1992b), which compares well with boiling point data for 111 organic compounds at pressures of 0.007, 0.08, 1, and 10-atm, and has the following form:

$$P_n^* = 87100 \cdot \exp\left(\frac{-299 \cdot M_n^{0.5903}}{T}\right)$$
(8.5)

where P_n^* is the vapor pressure of the pure nth-polymer fragment in atmospheres, MW_n is the molecular weight of the nth-polymer fragment in gm/mol, and T is the absolute temperature in K. The functional form of Equation 8.5 is similar to the Clausius-Clapeyron equation. For the vapor pressures of the light molecules, a correlation obtained from the DIPPR database (Rowley et al., 2002) is used, which has the following form:

$$P_1^* = \exp\left[a_1 + a_2/T + a_3 \cdot \ln(T) + a_4 \cdot T^{a_5}\right]$$
(8.6)

where P_1^* is the vapor pressure of the pure light molecule in Pascals, *T* is the absolute temperature in K, and a_1 , a_2 , a_3 , a_4 , and a_5 are fitted parameters for each of the light molecules.

The separation of the condensed phase into the solid, or non-flowing phase, and the liquid, or the flowing phase, is the next step. There are many factors to consider in this calculation. The transition point is not only a function of the molecular weight, but also a function of the structure and the number of cross-links for a given polymer fragment. Also, what may be deemed as "solid" may be soluble in the "liquid" phase and therefore can be transported with the liquid flow from the control volume. For the current polyurethane foam calculations, the solid phase was considered to be only the infinite polymer, while the remaining condensed phase was considered to be liquid. The infinite polymer was assumed to be insoluble in the liquid phase.

Non-Ideal Gas Behavior

At high pressures and low temperatures, the deviation from the ideal gas law can be significant. To account for this possibility, compressibility factors are used to correct the ideal gas law as seen below.

$$PV_m = ZR_o T \tag{8.7}$$

The compressibility factor (Z) is calculated using the Lee-Kesler equation of state (Walas, 1985). For the control volume, the volume and temperature are known for the specific time step. For the totally- and partially-confined cases, since the total mass in the cell is known, the pressure is updated to include the compressibility effects. Since the pressure of the cell is fixed for the unconfined case, the final mass of the gas phase is updated to include the compressibility effects.

Some of the experiments conducted were at pressure at 50 or 70 atmospheres, while the temperature ranged from 20-600°C. Compressibility of a gas is most important at high reduced pressures and low reduced temperatures. The average critical pressure of the polyurethane foam decomposition products is around 46 atm, while the critical temperature is around 700°C. This means that the reduced pressure is around 1.0-1.5 while the reduced temperature ranges from 01 to 0.9, causing the possibility for the compressibility to be important.

To utilize the Lee-Kesler equation of state, the critical temperature, critical pressure and accentric factor must be of the overall gas mixture. The Lee-Kesler-Plöcker mixing rules (Plocker et al., 1978) were used to determine the critical pressure (P_{cm}) critical temperature (T_{cm}) and accentric factor (\mathbf{w}_m) of the overall mixture in the gas phase, from the properties of the individual species in the gas phase. The critical

temperatures (T_{ci}) , critical pressures (P_{ci}) and accentric factors (\mathbf{w}_i) of the light molecules can be found in the DIPPR database, or any other source. The critical temperatures, critical pressures and accentric factors of the nth-polymer fragments are estimated.

The equation to calculate the accentric factor of the mixture from the accentric factor of the individual species is shown below:

$$\boldsymbol{w}_m = \sum_i y_i \boldsymbol{w}_i \tag{8.8}$$

where y_i is the mole fraction of species i in the mixture, and w_i is the accentric factor of species i. Next, the critical temperature of the mixture and critical molar volume of the mixture are calculated:

$$V_{cm} = \sum_{i} \sum_{j} y_{i} y_{j} V_{cij}$$
(8.9)

$$T_{cm} = V_{cm}^{-0.25} \sum_{i} \sum_{j} y_{i} y_{j} V_{cij}^{0.25} T_{cij}$$
(8.10)

where

$$T_{cij} = \sqrt{T_{ci}T_{cj}} \tag{8.11}$$

$$V_{cij} = \frac{1}{8} \left(V_{ci} \frac{V_3}{3} + V_{cj} \frac{V_3}{3} \right)^3$$
(8.12)

$$V_{ci} = \frac{Z_{ci}R_g T_{ci}}{P_{ci}}$$
(8.13)

$$Z_{ci} = 0.2905 - 0.085 \mathbf{w}_i \tag{8.14}$$

The parameters Z_{ci} , P_{ci} , T_{ci} , and V_{ci} are the critical compressibility factor, pressure, temperature, and molar volume of species i, respectively.

Finally the critical pressure and critical compressibility factor of the mixture (Z_{cm}) can be calculated by:

$$P_{cm} = \frac{R_g T_{cm} Z_{cm}}{V_{cm}}$$
(8.15)

$$Z_{cm} = 0.2905 - 0.085 \mathbf{w}_m \text{ or } Z_{cm} = \sum_i y_i Z_{ci}$$
(8.16)

The Lee-Kesler equation of state is based on the reduced temperature (T_r) and the reduced molar volume (V_r) as seen below.

$$Z = Z^{(0)} + \boldsymbol{w}_m Z^{(1)} \tag{8.17}$$

where

$$Z^{(1)} = \left(Z^{(r)} - Z^{(0)}\right) / \boldsymbol{w}^{(r)}$$
(8.18)

$$Z^{j} = 1 + \frac{B^{j}}{V_{r}} + \frac{C^{j}}{V_{r}^{2}} + \frac{D^{j}}{V_{r}^{5}} + \frac{c_{4}^{j}}{T_{r}^{3}V_{r}^{2}} \left(\boldsymbol{b}^{j} + \frac{\boldsymbol{g}^{j}}{V_{r}^{2}} \right) \exp\left(-\frac{\boldsymbol{g}^{j}}{V_{r}^{2}}\right)$$
(8.19)

$$B^{j} = b_{1}^{j} - b_{2}^{j} / T_{r} - b_{3}^{j} / T_{r}^{2} - b_{4}^{j} / T_{r}^{3}$$
(8.20)

$$C^{j} = c_{1}^{j} - c_{2}^{j} / T_{r} + c_{3}^{j} / T_{r}^{3}$$
(8.21)

$$D^{j} = d_{1}^{j} + d_{2}^{j} / T_{r}$$
(8.22)

$$V_r = \frac{V_m P_{cm}}{R_g T_{cm}}$$
(8.23)

$$T_r = \frac{T}{T_{cm}}$$
(8.24)

where j can be either the superscript (0), which stands for simple fluids, or the superscript (r), which stands for reference fluids. The two Z values are calculated with the different constants shown below in Table 8.1.

Constant	Simple Fluids	Reference Fluids
Collstant	j = (0)	j = (r)
b_1^{j}	0.1181193	0.2026579
b_2^{j}	0.265728	0.331511
b_3^{j}	0.154790	0.027655
$b_4{}^j$	0.030323	0.203488
$c_1^{\ j}$	0.0236744	0.0313385
c_2^{j}	0.0186984	0.0503618
c_3^{j}	0.0	0.016901
c_4^{j}	0.042724	0.041577
$d_1^{j} \times 10^4$	0.155488	0.48736
$d_{2}^{j} \times 10^{4}$	0.623689	0.0740336
b ^j	0.65392	1.226
g ^j	0.060167	0.03754

 Table 8.1
 Constants used in Lee-Kesler Correlation

For a typical polyurethane decomposition experiment at 50 atmospheres in helium, the compressibility ranged from 0.9 to 1.01, and so was significant in the calculations.

Outlet Flow Mass

For the unconfined case, since the control volume and the pressure are constant, as the temperature rises, the mass of the gas in the control volume decreases. Conversely, as the temperature rises and more bridges break, the generation of gas in the control volume increases, due to the increase in vaporized species. To keep the mass of the gas in the control volume consistent with the density, temperature, pressure and volume of the system, the adjusted mass of the gas is calculated from a gas law, modified by the compressibility factor. The mass of the outlet flow gas is then calculated through a gas phase mass balance as seen below in Equation 8.25:

$$M_{g}^{out} = M_{g}^{in} + M_{g} - M_{g}^{a}$$
(8.25)

There is no outlet flow of the condensed phase for the unconfined case.

For the partially-confined case with an orifice, the outlet flow of gas is calculated from an equation based on compressible flow theory:

$$M_{g}^{out} = C_{orf} \cdot A_{orf} \cdot P_{\sqrt{\frac{2g}{R_{g}T(g-1)}}} \left[\left(\frac{P_{amb}}{P} \right)^{1/g} - \left(\frac{P_{amb}}{P} \right)^{g+1/2g} \right]$$
(8.26)

where C_{orf} is a coefficient used to account for the losses through an orifice, A_{orf} is the area of the orifice, g is the ratio of specific heats, and P_{amb} is the ambient pressure outside the control volume. If the pressure in the control volume continues to increase, eventually the orifice will be choked. In that case the outlet flow gas is calculated by:

$$M_g^{out} = C_{orf} \cdot A_{orf} \cdot P_{\sqrt{\frac{g}{R_g T}}} \left(\frac{2}{g+1}\right)^{g+1/2(g-1)}$$
(8.27)

The deciding factor between these two equations is the ratio of the ambient pressure outside the control volume and the control volume pressure. Once the ratio drops to a critical value, seen below in Equation 8.28, the flow becomes choked. If the ratio rises above the critical value, the flow is no longer choked.

choked flow if
$$\frac{P_{amb}}{P} \le \left(\frac{2}{g+1}\right)^{g_{g-1}}$$
 (8.28)

There is no outlet flow of condensed phase for the partially-confined case.

For the totally-confined case, the flow rates of the gas and condensed phase leaving the system are simply zero. The flow rates of the gas and condensed phase leaving the system are calculated from the continuity and momentum equations for the general case. The outlet flow masses of the individual species (M_i^{out}) are then calculated by multiplying the weight fraction of the gas and condensed phases of each species by the total outlet flow mass of the gas and condensed phase. This assumes that the outlet flow gas and condensed phase has the same composition as in the computational cell (i.e., that the cell is well-mixed).

Mass to Population Conversion

The masses of the various species need to be converted to population variables for use in the bridge reactions. The challenge is to convert the mass of n-mers that left or entered the control volume, to site, bridge and side chain populations. This can be calculated through some conversion factors that can be derived from percolation lattice statistics. Recalling Equation 7.1, the molecular weight of an n-mer is:

$$MW_n = n \cdot MW_{sit} + s \cdot MW_{brg} + t \cdot MW_{sch}$$
(8.29)

The second term represents the mass of the bridges in the n-mer per mole of the n-mer. Dividing the second term in Equation 8.29, by the molecular weight of the n-mer produces:

$$\frac{M_n^{brg}}{M_n} = \frac{s \cdot MW_{brg}}{MW_n}$$
(8.30)

which is the mass of the bridges in the n-mer (M_n^{brg}) per mass of the n-mer (M_n) . Dividing this ratio by the molecular weight of the bridge yields:

$$\frac{mol_n^{brg}}{M_n} = \frac{s \cdot MW_{brg}}{MW_n \cdot MW_{brg}} = \frac{s}{MW_n}$$
(8.31)

which is the moles of the bridges in the n-mer (mol_n^{brg}) per mass of the n-mer. Multiplying this ratio by the original, inlet flow, and outlet flow masses of the n-mer, gives the original, inlet flow, and outlet flow moles of bridges. Similarly, conversion factors for the side chains and sites can be developed, and are shown below.

$$\frac{mol_n^{sch}}{M_n} = \frac{\mathbf{t}}{MW_n}$$
(8.32)

$$\frac{mol_n^{sit}}{M_n} = \frac{n}{MW_n}$$
(8.33)

Using these conversion factors, the amount of original, inlet flow, and outlet flow moles of bridges, side chains and sites for the n-mers can be determined. This however does not include the moles of bridges, side chains and sites in the infinite matrix.

The moles of bridges, side chains and sites in the infinite matrix can be calculated from a modified fraction of intact bridges. In general, bridge reactions occur both in the infinite matrix, as well as in the detached oligomers. Equations from percolation lattice statistics can be manipulated to generate the fraction of intact bridges for just the infinite matrix (p_{inf}). The variable p_{inf} is a function of the overall fraction of intact bridges in the system (p) and the coordination number (s + 1). In effect, the basis used to calculate the fraction of intact bridges is changed from both the infinite matrix and the oligomers, to just the infinite matrix.

The fraction of intact bridges in the infinite matrix (p_{inf}) can be calculated by dividing the moles of intact bridges in the infinite matrix per site (mol_{inf}^{brg}) by the total possible bridges per site in the infinite matrix. The total possible bridges per site in the

infinite matrix are the product of (s + 1)/2 and the fraction of sites contained in the infinite matrix (F_{inf}).

$$p_{\rm inf} = \frac{mol_{\rm inf}^{brg}}{\frac{s+1}{2} \cdot F_{\rm inf}}$$
(8.34)

The mol_{inf}^{brg} term can be calculated by the difference between the total moles of intact bridges in the system per site and the moles of intact bridges per site in the finite oligomers (mol_n^{brg}) . The total moles of intact bridges in the system per site is calculated by multiplying the p (which is on a per bridge basis) by (s + 1)/2 (which converts from a per bridge basis to a per site basis):

$$mol_{\inf}^{brg} = \frac{\mathbf{s}+1}{2} \cdot p - \sum_{n} mol_{n}^{brg}$$
(8.35)

The mol_n^{brg} term can be calculated from the product of the fraction of sites contained in the n-mer (F_n , see Equation 2.18) and the moles of bridges per site for an n-mer ($\frac{n-1}{n}$):

$$mol_n^{brg} = F_n \cdot \frac{n-1}{n} \tag{8.36}$$

Substituting Equations 8.35 and 8.36 into Equation 8.34 yields:

$$p_{\rm inf} = \frac{p - \frac{2}{\mathbf{s} + 1} \sum_{n} F_n \cdot \frac{n - 1}{n}}{F_{\rm inf}}$$

$$\tag{8.37}$$

which is only a function of p and the coordination number, since F_n and F_{inf} are only functions of p and the coordination number. As the value of p decreases to the value of p_{crit} , the value of p_{inf} approaches 2/(s+1). If the cut-off point technique is used, the value of p_{inf} approaches $[2/(s+1)] \cdot [n_{max}/(n_{max}+1)]$, as p approaches p_{crit} . This can be seen below in Figure 8.2, where p_{inf} versus p is plotted as a function of the cut-off point. As the cut-off point increases, the p_{inf} levels off earlier as seen in Figure 8.2.



Figure 8.2 p_{inf} (includes only infinite matrix) versus p (includes infinite matrix and detached fragments that originated in the cell) for various n_{max} . (s+1=3)

The fraction of intact bridges existing only in the infinite matrix can be used to calculate a molecular weight of an extended site, similar to Equation 7.4, but now of only the infinite matrix (m_{site}^{inf}) .

$$m_{site}^{\inf} = MW_{sit} + p_{\inf} \cdot MW_{brg} \cdot \frac{(\boldsymbol{s}+1)}{2} + (1-p_{\inf}) \cdot MW_{sch} \cdot (\boldsymbol{s}+1)$$
(8.38)

With the molecular weight of an extended site in the infinite matrix, the moles of sites, bridges and side chains in the infinite matrix can be easily calculated. The moles of sites in the infinite matrix (Mol_{inf}^{sit}) are equal to the moles of extended sites in the infinite matrix (Mol_{inf}^{exsit}) :

$$Mol_{\inf}^{sit} = Mol_{\inf}^{exsit} = \frac{M_{\inf}}{m_{site}^{\inf}}$$
(8.39)

The moles of bridges in the infinite matrix (Mol_{inf}^{brg}) are (s + 1)/2 times the moles of sites in the infinite matrix, multiplied by the fraction of intact bridges in the infinite matrix (p_{inf}) :

$$Mol_{\inf}^{brg} = Mol_{\inf}^{sit} \cdot p_{\inf} \cdot (\mathbf{s}+1)/2$$
(8.40)

The moles of side chains in the infinite matrix (Mol_{inf}^{sch}) are (s + 1)/2 times the moles of sites in the infinite matrix, multiplied by the fraction of broken bridges in the infinite matrix $(1 - p_{inf})$:

$$Mol_{\inf}^{sch} = Mol_{\inf}^{sit} \cdot (1 - p_{\inf}) \cdot (\mathbf{s} + 1)/2$$
(8.41)

With the conversion factors to calculate the moles of sites, bridges and side chains for the oligomers and the infinite matrix, the total inlet flow, outlet flow and previous moles of the various species can be calculated. The populations of the sites, bridges and side chains are then modified by two methods. Method one involves calculating the current number density of the various species and normalizing by the initial number density (discussed in Chapter 6). Method two uses the ratio of the current moles to the previous moles to obtain the current populations from the previous populations. Both methods work very well, but method two can have problems if the denominator of the ratio is zero.

The distribution of the various species in the gas and condensed phases can be calculated with all of the above equations in this chapter. The inlet flow and outlet flow of the various species from the gas and condensed phases can be calculated with the distribution of species in the gas and condensed phases. The population of the various species remaining in the cell is then updated for the inlet and outlet flow through the derived conversion factors.

Chapter 9. Model Parameter Determination

A summary of the equation that will be used in the MTPUF model is shown first in this chapter. The various parameters used in the model are discussed next. The different parameters that were fixed in the model are presented, along with any techniques used to estimate some of the parameters. A discussion is given of the parameters that were allowed to vary in the model. Finally, the techniques applied during the parameter optimization are illustrated.

Model Equation Summary

Many different techniques and algorithms have been discussed in the previous chapters. Here, a summary of these techniques, and how they relate to each other in the MTPUF model will be presented. The overall mass balance for a continually stirred reactor is:

$$\frac{dM_{tot}}{dt} = \dot{M}_{tot}^{in} - \dot{M}_{tot}^{out}$$
(9.1)

The mass balance equation for the species in the MTPUF model for a continually stirred reactor are shown in Table 9.1. The equations shown are in the units of gram per sec, while the generation terms have populations per sec for units. To convert the generation terms to a mass basis, conversion factors (discussed earlier) from percolation lattice statistics are used.

Species	Equation	Generation term
	$\frac{dM_{L_1}}{dt} = \dot{M}_{L_1}^{in} - \dot{M}_{L_1}^{out} + \dot{M}_{L_1}^{gen}$	$-k_1 \cdot L_1 + k_2 \cdot D_1 \cdot D_2 - k_5 \cdot L_1$
	$\frac{dM_{L_2}}{dt} = \dot{M}_{L_2}^{in} - \dot{M}_{L_2}^{out} + \dot{M}_{L_2}^{gen}$	$+k_5 \cdot L_1 - k_6 \cdot L_2 + k_7 \cdot D_2 \cdot D_3 - k_8 \cdot L_2$
L_3	$\frac{dM_{L_3}}{dt} = \dot{M}_{L_3}^{in} - \dot{M}_{L_3}^{out} + \dot{M}_{L_3}^{gen}$	$+ k_8 \cdot L_2 - k_9 \cdot L_3$
L_4	$\frac{dM_{L_4}}{dt} = \dot{M}_{L_4}^{in} - \dot{M}_{L_4}^{out} + \dot{M}_{L_4}^{gen}$	$-k_{11} \cdot L_4$
D_1	$\frac{dM_{D_1}}{dt} = \dot{M}_{D_1}^{in} - \dot{M}_{D_1}^{out} + \dot{M}_{D_1}^{gen}$	$ \begin{array}{l} + k_1 \cdot L_1 - k_2 \cdot D_1 \cdot D_2 - k_3 \cdot D_1 \\ + k_4 \cdot TDI \cdot D_2 \end{array} $
	$\frac{dM_{D_2}}{dt} = \dot{M}_{D_2}^{in} - \dot{M}_{D_2}^{out} + \dot{M}_{D_2}^{gen}$	$+ k_1 \cdot L_1 - k_2 \cdot D_1 \cdot D_2 + k_3 \cdot D_1$ $- k_4 \cdot TDI \cdot D_2 + k_6 \cdot L_2 - k_7 \cdot D_2 \cdot D_3$
<i>D</i> ₃	$\frac{dM_{D_3}}{dt} = \dot{M}_{D_3}^{in} - \dot{M}_{D_3}^{out} + \dot{M}_{D_3}^{gen}$	$+ k_6 \cdot L_2 - k_7 \cdot D_2 \cdot D_3$
D_4	$\frac{dM_{D_4}}{dt} = \dot{M}_{D_4}^{in} - \dot{M}_{D_4}^{out} + \dot{M}_{D_4}^{gen}$	$+ k_9 \cdot L_3 - k_{10} \cdot D_4$
D ₅	$\frac{dM_{D_5}}{dt} = \dot{M}_{D_5}^{in} - \dot{M}_{D_5}^{out} + \dot{M}_{D_5}^{gen}$	$+ k_9 \cdot L_3 + k_{10} \cdot D_4 + k_{11} \cdot L_4$
D ₆	$\frac{dM_{D_6}}{dt} = \dot{M}_{D_6}^{in} - \dot{M}_{D_6}^{out} + \dot{M}_{D_6}^{gen}$	$+ k_{11} \cdot L_4$
S_1	$\frac{dM_{S_1}}{dt} = \dot{M}_{S_1}^{in} - \dot{M}_{S_1}^{out}$	-
<i>S</i> ₂	$\frac{dM_{S_2}}{dt} = \dot{M}_{S_2}^{in} - \dot{M}_{S_2}^{out}$	-
TDI	$\frac{dM_{TDI}}{dt} = \dot{M}_{TDI}^{in} - \dot{M}_{TDI}^{out} + \dot{M}_{TDI}^{gen}$	$+k_3 \cdot D_1 - k_4 \cdot TDI \cdot D_2$
TDA	$\frac{dM_{TDA}}{dt} = \dot{M}_{TDA}^{in} - \dot{M}_{TDA}^{out} + \dot{M}_{TDA}^{gen}$	$+k_{10}\cdot D_4$
CPN	$\frac{dM_{CPN}}{dt} = \dot{M}_{CPN}^{in} - \dot{M}_{CPN}^{out} + \dot{M}_{CPN}^{gen}$	$+ k_{11} \cdot L_4$
<i>CO</i> ₂	$\frac{dM_{CO_2}}{dt} = \dot{M}_{CO_2}^{in} - \dot{M}_{CO_2}^{out} + \dot{M}_{CO_2}^{gen}$	$+k_5 \cdot L_1 + k_8 \cdot L_2 + k_{11} \cdot L_4$

Table 9.1General equation set for the MTPUF model.

As seen in Table 9.1, the species mass balances all have the same form, except for the site equations, which do not have generation terms. This comes from the fact that the sites

are not generated due to the reactions. The overall rate of inlet and outlet mass flow is calculated differently for the various stages of confinement. For the unconfined case, the inlet flow mass term is calculated from the recirculation and diffusion flow terms, while a gas law and diffusion flow terms are used to calculate the outlet flow mass term. For the partially-confined case, the inlet flow mass term is calculated from the diffusion flow term, while the outlet flow mass term is calculated from compressible theory. There is no flow in or out for the totally-confined case. For the general case, the flow in and out of the cell would be calculated from the continuity and momentum equations.

Knowing the total mass in and out of the cell, the rate of mass in and out for the individual species is calculated by:

$$\dot{M}_{i}^{in} = \dot{M}_{tot}^{in} \cdot \sum_{n=1}^{n_{max}} w_{n-mer}^{in} \cdot \frac{M_{n-mer}^{i}}{M_{n-mer}}$$
(9.2)

$$\dot{M}_{i}^{out} = \dot{M}_{tot}^{out} \cdot \sum_{n=1}^{n_{max}} w_{n-mer}^{out} \cdot \frac{\dot{M}_{n-mer}^{i}}{M_{n-mer}}$$
(9.3)

where the i represents the various bridges, side chains and sites. The ratio in the summations in Equations 9.2 and 9.3 are the conversion factors discussed in Chapter 8. A summary of the conversion factors to calculate the moles or mass of the various bridges, side chains and sites from the mass of the n-mer or the infinite matrix are shown in Table 9.2. The second column shows the conversion of the mass of the n-mer or infinite matrix to the mass of the various species (i.e., bridges, side chains or site), while the third column shows the conversion of the mass of the n-mer or infinite matrix to the moles of the various species.

Conversion Factor	Mass of species	Moles of species
Bridges contained in an n-mer	$\frac{M_n^{brg}}{M_n} = \frac{s \cdot MW_{brg}}{MW_n}$ (Equation 8.30)	$\frac{mol_n^{brg}}{M_n} = \frac{s}{MW_n}$ (Equation 8.31)
Side chains contained in an n-mer	$\frac{M_n^{sch}}{M_n} = \frac{\boldsymbol{t} \cdot MW_{sch}}{MW_n}$	$\frac{mol_n^{brg}}{M_n} = \frac{t}{MW_n}$ (Equation 8.32)
Sites contained in an n-mer	$\frac{M_n^{sit}}{M_n} = \frac{n \cdot MW_{sit}}{MW_n}$	$\frac{mol_n^{sit}}{M_n} = \frac{n}{MW_n}$ (Equation 8.33)
Bridges contained in the infinite matrix	$\frac{M_{\inf}^{brg}}{M_{\inf}} = \frac{MW_{brg} \cdot p_{\inf} \cdot (\mathbf{s}+1)/2}{m_{site}^{\inf}}$	$\frac{mol_{inf}^{brg}}{M_{inf}} = \frac{p_{inf} \cdot (s + 1)/2}{m_{site}^{inf}}$ (see Equation 8.40)
Side chains contained in the infinite matrix	$\frac{M_{\inf}^{sch}}{M_{\inf}} = \frac{MW_{sch} \cdot (1 - p_{\inf}) \cdot (\mathbf{s} + 1)/2}{m_{site}^{\inf}}$	$\frac{mol_{\inf}^{brg}}{M_{\inf}} = \frac{(1 - p_{\inf}) \cdot (\mathbf{s} + 1)/2}{m_{site}^{\inf}}$ (see Equation 8.41)
Sites contained in the infinite matrix	$\frac{M_{\inf}^{sit}}{M_{\inf}} = \frac{MW_{sit}}{m_{site}^{\inf}}$	$\frac{mol_{inf}^{sit}}{M_{inf}} = \frac{1}{m_{site}^{inf}}$ (See Equation 8.39)

Table 9.2Summary of the conversion factors used to convert the mass of the
oligomers or infinite matrix to the mass or moles of the bridges, side
chains and sites.

The weight fraction of either a light molecule or an n-mer, denoted by i, is calculated by:

$$w_{i}^{out} = \frac{w_{i}^{g} \cdot \dot{M}_{g}^{out} + w_{i}^{c} \cdot \dot{M}_{c}^{out}}{\dot{M}_{g}^{out} + \dot{M}_{c}^{out}}$$
(9.4)

The w_{n-mer}^{in} would be calculated as the w_{n-mer}^{out} from a neighboring computational cell, and would have the same form as Equation 9.4. The w_i^g and w_i^c are calculated from the overall weight fraction in the cell (w_i) through an isothermal flash calculation. The algorithm used for the isothermal flash is shown in Figure 9.1. After the isothermal flash, the gas properties are modified by the compressibility factor calculations.



Figure 9.1 Algorithm used for the isothermal flash calculations.

The Fletcher-Grant-Pugmire (FGP) vapor pressure correlation (Fletcher et al., 1992a; 1992b) is used to compute the values of the vapor-liquid equilibrium ratio (K) for the oligomers, while the DIPPR vapor pressure correlation (Rowley et al., 2002) is used to compute the vapor-liquid equilibrium ratios for the light molecules. With the K values and the overall mole fractions (z) for each species, the Rachford-Rice (Rach-Rice) equation (Seader and Henley, 1998) is then used to calculate the split between the vapor and condensed phase (V/F). The infinite matrix is excluded from the isothermal flash calculations, since in this case, it is treated as a solid that does not interact with the condensed or vapor phase. With the value of V/F, the condensed phase mole fraction (x),

and the gas phase mole fraction (y) can be calculated and then converted to a condensed phase weight fraction (w^c) and a gas phase weight fraction (w^g), respectively. The equations used in this process are summarized in Table 9.3.

-		
	$z_i = \frac{\frac{W_i}{MW_i}}{\sum_{i=1}^{W_i} MW_i}$	
Oligomers	$K_i = 87100 \exp\left(\frac{-299MW_i^{0.59}}{T}\right) / P$ (Equation 8.5)	
Light Molecules	$K_{i} = \exp\left[a_{1} + a_{2}/T + a_{3} \cdot \ln(T) + a_{4} \cdot T^{a_{5}}\right]/P$ (Equation 8.6)	
$0 = \sum_{i=1}^{n} \frac{z_i (K_i - 1)}{(K_i - 1) \frac{V}{F} + 1} $ (Equation 8.1)*		
	$x_i = \frac{z_i}{\left(K_i - 1\right)\frac{V}{F} + 1}$ (Equation 8.3)	
$y_i = \frac{K_i z_i}{(K_i - 1)\frac{V}{F} + 1}$ (Equation 8.4)		
$w_i^c = \frac{x_i \cdot MW_i}{\sum x_i \cdot MW_i}$		
$w_i^g = \frac{y_i \cdot MW_i}{\sum y_i \cdot MW_i}$		

 Table 9.3
 Summary of equations used in the isothermal flash calculations.

* Solved for the value of V/F

The mass fraction of each species (w_i) is calculated from the mass of each species (M_i) . The mass of each species is calculated from the mass of the species in the cell from the previous time step $(M_i^{(t-\Delta t)})$ and the change in bridge population (dp) for

when bridges break, and using the change in the side chain population (dsc) for when bridges are forming. The values of dp and dsc are computed from the population variables. The equations derived in the population balance theory (Equations 7.9-7.10, 7.15, 7.20-7.32) for the oligomers and the infinite matrix are used to calculate the new distribution of the products. The algorithm used for the population balance theory is shown in Figure 9.2.



Figure 9.2 Algorithm used in the population balance theory calculations.

The population balance (Pop-Bal) theory equations calculate the current moles of the various oligomers in the cell (*mol*) from the mole of the various oligomer in the cell at the previous time step ($mol^{(t-\Delta t)}$), which are then converted to the mass in the cell (*M*). The algorithm is the same whether the bridges are being formed or broken, but the equations used in the population balance theory are different. A summary of the equations used in the population balance theory calculations is shown in Table 9.4.

$mol_n^{(t-\Delta t)} = \frac{M_n^{(t-\Delta t)}}{MW_n}$			
Bridge Breaking	$dp = 1 - \frac{L_1^{(t-\Delta t)} + L_2^{(t-\Delta t)} + L_3^{(t-\Delta t)} + L_4^{(t-\Delta t)}}{L_1 + L_2 + L_3 + L_4} $ (Equation 7.9)		
	$\frac{mol_{n\to m}}{mol_n} = \sum_{br=0}^{n-1} C_{nmbr} (dp)^{br} (1-dp)^{n-1-br} \text{(Equation 7.10)}$		
	$ \begin{pmatrix} (br+1) \cdot \binom{n-m-1}{br-1} & m \le n-br, br \ge 1 \end{cases} $		
	$0 \qquad m > n - br, br \ge 1$		
	$C_{nmbr} = \begin{cases} (Equation 7.11) \\ 1 & m = n, br = 0 \end{cases}$		
	$0 m \neq n, br = 0$		
	$dsc = \frac{2 \cdot \left[\left(L_1 + L_2 + L_3 + L_4 \right) - \left(L_1^{(t - \Delta t)} + L_2^{(t - \Delta t)} + L_3^{(t - \Delta t)} + L_4^{(t - \Delta t)} \right) \right]}{2}$		
	$D_1 + D_2 + D_3 + D_4 + D_5 + D_6$		
	(Equation 7.15)		
	$t_n = n(s - 1) + 2$ (Equation 7.16)		
Bridge Forming	$\frac{mol_n^0}{mol_n} = (1 - dsc)^{t_n} \text{(see Equation 7.17)}$		
	$mol^{gen} = \frac{1 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot (1 - dsc)^{\boldsymbol{t}_i + \boldsymbol{t}_j - 2} \cdot dsc^2 \cdot mol_i \cdot mol_j}{1 - dsc^2 \cdot mol_i \cdot mol_j}$		
	tot^{fr} (Equation 7.22)		
	$mol_{sen}^{gen} = \frac{2 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot (1 - dsc)^{\boldsymbol{t}_i + \boldsymbol{t}_j + \boldsymbol{t}_k - 4} \cdot dsc^4 \cdot mol_i \cdot mol_j \cdot mol_k}{dsc^4 \cdot mol_i \cdot mol_j \cdot mol_k}$		
	$(tot^{fr})^2$		
	(see Equations 7.23, 7.29-7.30)		
$M_n = mol_n \cdot MW_n$			

 Table 9.4
 Summary of equations used in the population balance theory calculations.
As seen in Table 9.4, the equations used for bridge breaking and for bridge forming are different, but they use similar variables.

Fixed Parameters

Many of the input parameters for the MTPUF model were fixed, or did not change once their value was initially calculated. These parameters include the initial populations of the various species, as well as the vapor pressure parameters. The critical properties of the various species were either found in or estimated from the literature. The flow parameters were estimated with computational fluid dynamic modeling and correlations. The values of the parameters are discussed in more detail below.

Initial Populations

The first set of parameters that were fixed in the model is the initial populations of the different sites, bridges, side chains and light molecules. Table 9.4 shows the initial populations of the various sites, bridges, side chains and light molecules. The initial populations for the bridges, side chains and light molecules were determined from the molar ratio of the bridges, side chains and light molecules in the initial polyurethane foam structure (see Figure 1.1). The initial population for the sites was determined from a mole ratio of the sites in the initial polyurethane foam structure (see Figure 1.1). The initial polyurethane foam structure (see Figure 1.1). The species are also shown in Table 9.5. The various symbols used in Table 9.5 are the same symbols defined in Figure 6.4.

Symbol	Initial	Molecular	Symbol	Initial	Molecular
, , , , , , , , , , , , , , , , , , ,	Population	Weight		Population	Weight
D_1	0.00	205	L_1	0.78	236
D_2	0.00	31	L_2	0.00	192
D_3	0.00	161	L_3	0.00	148
D_4	0.00	134	L_4	0.22	172
D_5	0.00	14	TDI	0.00	174
D_6	0.00	30	TDA	0.00	120
S_1	0.78	41	CPN	0.00	84
\overline{S}_2	0.22	44	CO_2	0.00	44

Table 9.5Initial populations for the sites, bridges, side chains and light molecules.

Vapor Pressure Coefficients

The vapor pressure coefficients for the light molecules were the next set of parameters that were fixed in the model. These coefficients are used in determining the vapor pressure of the light molecules (as discussed in Chapter 8), and used in the following equation:

$$P_{I}^{*} = \exp\left[a_{1} + a_{2}/T + a_{3} \cdot \ln(T) + a_{4} \cdot T^{a_{5}}\right]$$
(8.6)

The vapor pressure parameters were obtained from the DIPPR database (Rowley et al., 2002). Table 9.6 shows the parameters for the various light molecules.

Parameter	TDI	TDA	CPN	CO_2	
a_1	194.22	75.248	56.405	140.54	
a_2	-14314	-11094	-6444.5	-4735	
a_3	-26.701	-6.9328	-4.8222	-21.268	
a_4	2.2518×10 ⁻²	7.8095×10 ⁻¹⁹	4.8774×10 ⁻¹⁸	4.0909×10 ⁻²	
<i>a</i> ₅	1.0	6.0	6.0	1.0	

 Table 9.6
 Vapor pressure coefficient for the light molecules.

The critical properties of the various species were also fixed in the model. The critical properties of the monomers, dimers, trimers, etc., were estimated in the CPUF model (Hobbs et al., 1999; 2000) and the same values were used in this project. The values were found to not be important, since the concentrations of the monomers, dimers, trimers, etc. in the gas phase were not significant, but still are needed for the computations. Table 9.7 shows the critical properties of the various species that are in the MTPUF model.

Creation	Critical	Critical	Accentric
Species	Temperature (K)	Pressure (atm)	Factor
TDI	725	30.0	0.433782
TDA	804	43.2	0.579439
CPN	625	45.4	0.287647
	304	72.9	0.223621
Monomer	800	46.0	0.4
Dimer	800	46.0	0.4
Trimer +	800	46.0	0.4
Infinite Matrix	800	46.0	0.4
He	5.2	2.25	-0.3903
N ₂	126.2	33.6	0.037722

Table 9.7Critical properties used in MTPUF model.

Flow Parameters

The inlet flow parameters were the final set that were fixed in the model. The inlet flow was treated as coming from two sources, a recirculation eddy and diffusion. During the modeling, the recirculation eddy flow was only considered present for the unconfined experiments, since the lid would have eliminated a recirculation eddy. The diffusion flow was considered in both the unconfined and the partially-confined cases.

Recirculation Flow

To obtain the magnitude of the recirculation eddy flow, the HPTGA flow patterns were modeled with a commercially available CFD (computational fluid dynamics) software named Fluent. A graphic of the grid for the modeling is shown in Figure 9.3. The system was treated as an axi-symmetric system, with the axis of symmetry on the bottom.



Figure 9.3 Grid setup for modeling the flow in the HPTGA.

The solid black area represents the solid basket holding the sample, while the solid gray area represents the foam sample. The solid white area to the left of the sample and basket is the thermocouple cover and the thermocouple that measures the temperature near the sample. The entire area of the flow was setup into a triangular grid. There were 7456 triangular cells and 4098 nodes in the simulation.

The simulation of the flow in the HPTGA was conducted with both laminar and turbulent flow models. Both cases gave similar results. The flow patterns inside the HPTGA are shown below in Figure 9.4. The flow enters on the left and exits on the right of Figure 9.4.



Figure 9.4 Flow patterns in the HPTGA.

As seen in Figure 9.4, the flow expands between the thermocouple and the basket and then is compressed around the basket. The flow then accelerates past the basket and then expands. A small recirculation eddy is formed above the sample.

The mass flow was increased proportionally to the pressure during the experiments, since a higher flow of inert gas was needed to sustain a higher pressure. Higher flow and pressure conditions were modeled as well with Fluent. The shape of the flow did not change with a higher flow rate and pressure, but rather the mass flow rate of the recirculation eddy flow increased proportionally as the overall mass flow rate increased. To illustrate, at one atmosphere, the recirculation eddy flow was calculated to be 1.755×10^{-6} gm/sec, while at ten atmospheres, the recirculation eddy flow was calculated to be 1.755×10^{-5} gm/sec.

Diffusion Flow

The diffusion flow through the orifice for the partially confined experiments, or the top of the open basket for the unconfined experiment was calculated through the following equation.

$$\dot{M}_{dif}^{in} = A_{orf} \cdot MW_{inert} \cdot N_{inert}$$
(9.5)

where

$$N_{inert} = D_{inert, products} \cdot \frac{dc_{inert}}{dh}$$
(9.6)

 A_{orf} is the area of the orifice, and N_{inert} is the molar flux of the inert gas in through the orifice. The concentration gradient of the inert gas (dc_{inert}/dh) is estimated by calculating the concentration of the inert gas outside of the basket (100% inert gas) and inside the basket (~80% inert gas) and dividing by the an estimated gradient distance (80 μ m). The concentration of the inert gas inside the basket was recalculated at each time step.

The diffusivity of the inert gas into the decomposition product gases ($D_{inert, products}$) was estimated through a correlation that involves the critical properties and molecular weight of the various species. This correlation was developed from a combination of kinetic theory and corresponding-states arguments (Bird et al., 1960).

$$D_{AB} = 2.745 \times 10^{-4} \cdot \frac{(P_{cA} P_{cB})^{\frac{1}{3}}}{P} \cdot (T_{cA} T_{cB})^{\frac{5}{12}} \cdot \left(\frac{1}{MW_A} + \frac{1}{MW_B}\right)^{\frac{1}{2}} \cdot \left(\frac{T}{\sqrt{T_{cA} T_{cB}}}\right)^{1.823} (9.7)$$

where the subscript A refers to the inert gas and the subscript B refers to the foam decomposition product gases, and D_{AB} [=] cm²/sec, MW [=] gm/mol, P and P_c [=] atm, and T and T_c [=] K. The 2.745×10^{-4} term contains the remaining units to balance the equation. The critical properties of the product gas mixture are calculated from the Lee-Kesler-Plöcker mixing rules (Plocker et al., 1978) as discussed in Chapter 8. For example, the diffusivity of helium into a 50/50 mixture of TDI and monomer at 300 K is $0.48 \text{ cm}^2/\text{sec}$. This would correspond to a mass flow rate of inert gas into the cell of 7.488×10^{-6} gm/sec (orifice diameter = 4 mm, $dc_{inert}/dz = 7.76 \times 10^{-6} \text{ mol/cm}^4$). Furthermore, the TDI and monomer would flow out of the cell as well. If the orifice

diameter was reduced to 0.06 mm the mass flow rate of inert gas due to diffusion drops to 0.002×10^{-6} gm/sec. The diffusivity was recalculated at each time step, as the temperature and distribution of the gases products changed.

Variable Parameters

The parameters that were changed to fit the data were the kinetic parameters for the various reactions. Each reaction has a preexponential factor and activation energy. The problem can become very stiff when each parameter is varied independently. A technique that was used to reduce the stiffness of the problem involved changing the form of the preexponential factor by the following relationship:

$$A_i = 10^{b_i} \cdot \exp\left(\frac{E_i}{R_g \cdot T_o}\right)$$
(9.8)

where E_i is the activation energy for reaction i, b_i is the preexponential coefficient for reaction i, and T_o is a reference temperature. This causes the preexponential factor to change with the activation energy and reduces the stiffness. The result of this relationship can be illustrated by the following example. Plotting the logarithm of the rate of reactions 1, 2 and 3 each with different activation energies (30,000, 60,000, and 90,000 cal/mol), versus one over the temperature and setting the preexponential factor at 1.0×10^{33} gives the following plot. (see Figure 9.5). As seen in Figure 9.5, the rates of the various reactions are very different in the temperature range of 300-1000 K. Reaction 1 (30,000 cal/mol) has a very high rate compared to reaction 2 (60,000 cal/mol) and reaction 3 (90,000 cal/mol). This would cause the problem to be very stiff, since the reaction time for reaction 1 is much shorter than for reaction 2 or 3.



gure 9.5 Plot of log K versus 1/1 for three reactions with a coll preexponential factor (1.0×10^{33}) .

Recalculating the rates of reactions 1, 2 and 3 with a $b_i = 20$, gives the following plot. (Figure 9.6) A reference temperature (T_o) of 500 K was used in the calculations, giving the preexponential factors for reactions 1, 2 and 3 to be 1.3×10^{33} , 1.7×10^{46} and 2.2×10^{59} , respectively. As seen in Figure 9.6, the reaction rates are much closer together, especially at a temperature of 500 K (T_o), where the rates are exactly the same. It is also noted that the rates at 500 K are all equal to 10^{20} , which comes from the parameter $b_i =$ 20. This technique is one way to reduce the stiffness of the problem, while allowing more flexibility in the activation energy.



Figure 9.6 Plot of log K versus 1/T for three reactions with an activation energy dependent preexponential factor ($b_i = 20, T_o = 500$ K).

The optimization technique used to find the kinetic parameters is called simulated annealing (Aarts and Korst, 1989; Bohachevsky et al., 1986; Kirkpatrick et al., 1983). The simulated annealing technique models the annealing of solid materials to optimize a complex system. The algorithm randomly perturbs the initial design. If the value of the objective function (variation from the data) is better, the new design is made the current design. If the value of the objective function is worse, the new design may still be accepted according to a probability factor. This allows the algorithm to escape local minima. This works well with kinetic parameters, since many local minima are found when obtaining kinetic parameters. During the optimization in this project, a reference temperature (T_o) of 1006.5 K was used. In this project, the activation energies (E_i) were

allowed to vary between 20,000 and 100,000 cal/mol, while the preexponential coefficients (b_i) were allowed to vary between 0 and 12.

The other two parameters that were allowed to vary during the modeling were the time step (dt) and the cut-off point (n_{max}) of the mer size. The time step was lowered until the results did not significantly change. The cut-off point was increased, until the results were not affected significantly. As the time step decreased, or the cut-off point increased, the computational time to obtain the results increased. A time step of 1.0 sec and a cut-off point of 6-mer were found to be computationally efficient, while achieving results independent of their values.

Chapter 10. Modeling Results

The results of the modeling are presented in this chapter. The final values of the kinetic parameters, and the data used in their determination are discussed first. Comparisons between the various temperature ramp data and modeling results are then shown. The isothermal experiments are compared with the model next. Likewise, the pressure dependence of the modeling results is contrasted with the trends in the data. The data from the confinement experiments are compared with the model predictions. Finally, possible explanations for the variation between the data and modeling results are discussed.

Kinetic Parameters

The kinetic parameters that were found through curve-fitting the atmospheric mass loss and product distribution data are shown in Table 10.1 for the 11 reactions. Using these parameters, the MTPUF model was then tested against the data obtained at elevated pressures and various degrees of confinement. With no adjustment to the parameters obtained from the atmospheric data, the model predicted the pressure and confinement effects very well. The model predictions for the various experiments with these kinetic parameters are shown in the following sections.

	Preexponential	Activation
Reaction	Factor (A _i)	Energy (E _i)
	[population/sec]	[cal/mol]
1	8.15×10^{14}	42,900
2	4.01×10^{14}	36,600
3	2.05×10^{14}	38,900
4	1.69×10^{11}	29,900
5	1.51×10^{11}	37,400
6	1.58×10^{8}	31,900
7	9.06×10^{10}	22,000
8	2.69×10^{10}	36,000
9	1.38×10^{8}	30,800
10	1.11×10^{10}	37,400
11	7.91×10^{16}	63,500

 Table 10.1
 Kinetic Parameters for the 11 polyurethane foam pyrolysis reactions.

As seen in Table 10.1, the activation energies for the various polyurethane foam pyrolysis reactions ranged from 22,000 to 64,000 cal/mol, while most of the reactions occurred around 35,000 cal/mol. This is in the expected range for all of the reaction (Hobbs et al., 1999; 2000).

To show how these kinetic parameters affected the transient behavior of the populations, the instantaneous populations of the bridges, side chains, sites and light molecules are shown below in Figure 10.1. The populations of the light molecules are multiplied by one thousand to be on the same scale as the other species. The predictions were made for the 20° C/min ramped experiments (1 bar). Bridge 1 (L₁) reacts first and forms bridge 2 (L₂) which then forms some bridge 3 (L₃) as seen in Figure 10.1a. Bridge 4 (L₄) slowly decreases and then drops to zero. Part of the decrease in the bridge population is due to reaction and the other part is due to flow out of the cell.



Figure 10.1 Populations of a) bridges, b) side chains, c) sites and d) light molecules versus time for a 20°C/min ramped experiment to 600°C. (1 bar)

The effect of the flow out can be seen in Figure 10.1c, where the populations of both sites $(S_1 \text{ and } S_2)$ is decreasing only due to flow, since the sites do not react in the chemical mechanism. Side chain 1 (D1) is formed first with side chain 2 (D2) as seen in Figure 10.1b. Side chain 3 (D3) does not have a significant population throughout the entire 30 minutes. Side chains 4 (D4) and 5 (D5) are formed next with side chain 6 (D6) being formed last. The populations of the side chains also all drop to zero at a time of about 23 minutes as most of the sites, bridges and side chains have been swept out of the computational cell. The populations of the light molecules is never very significant throughout the entire 30 minutes as seen in figure 10.1d. The sweeping out of the decomposition products mainly causes the populations of the light molecules to be low, since the light molecules vaporize much more readily than the monomers, dimers, etc.

Temperature Ramp Comparison

As discussed earlier in Chapter 2, one technique used to evaluate kinetic parameters obtained from thermogravimetric data is to compare the results from the parameters with various heating rates. Three different heating rates (10, 20 and 40 °C/min) were used while collecting the decomposition data on the HPTGA. A comparison of the heating ramp data and the results from the model for those conditions is shown in Figure 10.2. The data and results are plotted against temperature to give a better picture of the heating ramp dependence of the data and the modeling results.



experiments with the polyurethane foam. (1 atm)

As shown in Figure 10.2, the model matches the heating ramp data very well. Furthermore, the data show a shift in the temperature as the heating rate is increased. This trend is also predicted with the MTPUF model. The trend is a little over predicted around 300 and 400°C for the 40°C/min condition. One attribute of the model that does not compare well with the data is that the model shows the percent of sample remaining after ~450°C to be equal to zero instead of the 1% indicated from the data. This may indicate that the chemical mechanism does not include enough reactions to account for the formation of a small amount of carbonaceous residue.

Isothermal Comparison

Another technique that has been valuable in evaluating kinetic parameters derived from thermogravimetric data is to include not only heating ramp experiments, but isothermal experiments as well. Data from three different isothermal conditions (200, 300 and 400°C) were collected in the atmospheric experiments. A comparison of the isothermal data and the results from the model for those conditions is shown in Figure 10.3. The data and results are plotted versus time for best comparison. As indicated in Figure 10.3, the model results and the data agree very well throughout the entire two-hour period. The model slightly over predicts the decomposition at 30 minutes for 300°C isothermal experiment, while it slightly under predicts the decomposition for the 400°C



Figure 10.3 Comparison of modeling results and data for isothermal experiments with the polyurethane foam. (1 atm)

Comparison with Pressure Data

The pressure dependence of the HPTGA data indicates that as the pressure increases, higher temperatures are required to obtain the same decomposition. The model was tested versus the pressure data using the kinetic parameters determined from the atmospheric pressure data. None of the parameters were changed during the modeling of the high pressure experiments. A comparison of the model versus the data from the high pressure TGA experiments is shown in Figure 10.4.



Figure 10.4 Comparison of modeling results and data versus pressure for pressure experiments with the polyurethane foam.

As seen in Figure 10.4, the model does have the same trend as the data, but the magnitude of the shift is higher for the 10 bar and 30 bar conditions, and is a little low for the 50 bar condition. For a change in pressure from 1 to 50 atm, the shift in the data at 80% of the initial sample is 30° C, while the model only predicts 15° C. Likewise, the shift in the data at 40% of the initial sample is 60° C, while the model predicts 40° C. The model also does not totally explain the data in the later stages of pyrolysis for the pressurized experiments (i.e., at temperatures above 450° C).

The pressure dependence of the model was also checked versus the 300°C isothermal experiments and is shown in Figure 10.5. As seen in Figure 10.5, the pressure dependence matches very well through the entire run for the isothermal experiment.



Next, the pressure dependence of the product distribution predicted by the MTPUF model was compared with the available data. The main objective was to see if the model could predict the increase in the carbon dioxide (CO_2) production, and the decrease in the toluene diisocyanate (TDI) production, as seen in the data as pressure was increased. The product distribution with increasing pressure is shown in Figure 10.6. Oligomers with more than four sites (4-mers and higher) mainly stayed in the condensed phase, and hence are not shown in the pyrolysis product distribution.



Figure 10.6 Predicted decomposition product distribution with increasing pressure for the polyurethane foam. (20°C/min)

As seen in Figure 10.6, the model predicts that as the pressure increases, the production of carbon dioxide (CO₂) increases, while the toluene diisocyanate (TDI) production decreases. The percent of the sample released as carbon dioxide agrees fairly well with the data collected with the gas chromatograph. In the 1, 10 and 30 bar experiments, the percent of the sample that was released as carbon dioxide was 10, 12.5 and 18%, respectively. The MTPUF model predicted that in the 1, 10 and 30 atm experiments, the percent of the sample that was released as carbon dioxide was 5, 10 and 14%, respectively. It is also observed that as the pressure increases, the fraction of monomers increases while the fraction of dimers and higher decreases. It appears that the toluene diamine (TDA) and the cyclopentanone (CPN) production also increase as the pressure increases.

Comparison with Confinement Data

The partially-confined TGA data show that as the orifice size decreases, higher temperatures are required to obtain the same amount of decomposition. Using the kinetic parameters determined from the atmospheric pressure data, the model was then tested versus the confinement experiments. It was noted that the partially-confined experiments were conducted with a much different sample shape than the other TGA experiments. Instead of the thinly sliced samples, a much thicker sample was used. It was then noted during the experiments, that some inherent mass transfer effects where present with these partially-confined experiments. The experimental data from the 2 mm orifice size was very similar to the unconfined experimental data, except there was a shift in the reaction temperature. Conversely, very little difference was seen in the product distribution. A comparison of the model predictions with the partially-confined experiment data is shown in Figure 10.7. These modeling results were generated with an orifice coefficient (C_{orf}) of 1.0, and were corrected for the inherent mass transfer effects.

As the orifice sized decreases, the model shows the curve shifting to the higher temperatures, similar to the data. The model, however, predicts a much lower shift before 400°C and then a higher shift after 400°C than is seen in the data. For a decrease in the orifice size from 2 mm to 0.06 mm, the shift in the data at 80% of the initial sample is 35°C, while the model only predicts 22°C. Similarly, the shift in the data at 40% of the initial sample is 50°C, while the model predicts 65°C. This is very similar to the pressure trend of the MTPUF model.



experiments with polyurethane foam.

The change in the distribution of the decomposition products as the orifice size decreased was observed to further analyze the predictive capabilities of the MTPUF model. A plot of the decomposition product distribution as a function of orifice size is shown in Figure 10.8. Again, the 4 mers and above did not vaporize significantly at these conditions and hence are not shown in the distribution. As seen in Figure 10.8, the trends are very similar to the trends observed with increasing pressure. The model predicts that as the orifice size decreases, the production of carbon dioxide (CO_2) increases, while the toluene diisocyanate (TDI) production decreases. It is also observed that as the orifice size decreases, the fraction of monomers increases while the fraction of dimers and higher decreases. The MTPUF model also predicts that the toluene diamine (TDA) and the cyclopentanone (CPN) production increase as the orifice size decreases.



Figure 10.8 Predicted decomposition product distribution with decreasing orifice size for the polyurethane foam. (20°C/min)

To further test the confinement effects predicted by the MTPUF model, the totally-confined experiments were also modeled and compared with the data. Again, none of the kinetic parameters were changed during the modeling of the totally-confined experiments. The results are shown in Figure 10.9. As seen in Figure 10.9, the model agrees with the trends seen in the data very well. The model predictions are much coarser than the displacement data. This coarseness arose from the fact that the pressure data used in the model was very coarse. The pressure input was not modified to help smooth out the curve, to sustain the integrity of the modeling test. For both cases, there is an initial lag between the modeling results and the data from 45-80 minutes. One possibility for this difference is that initially the foam could support the load. Then, the gas pressure in the cells will be less than the load pressure. As the pressure in the cells

exceeds the load pressure, which appears to coincide with the loss of cell strength, the piston would then begin to displace. Modeling these initial effects is left to future researchers.



Figure 10.9 Comparison of the model results and data for the totally-confined experiments with polyurethane foam. (Data from Erickson, 2002)

Variation Explanations

There are many possible explanations for the variation between the various experiments and modeling results. Generally, all of the trends coincided for all of the conditions tested. The only variation came from the magnitude of the shift. Some shifts were too low, while others were too high. The variation in the prediction of the shifts may be caused from the fact that only the atmospheric pressure experiments were used to determine the kinetic parameters. The effect of the reversible reactions is not dominant at atmospheric pressure, and so while only a small error in the rates is observable at atmospheric pressure, the error in the kinetic parameters for the higher pressure or confinement experiments is more easily seen. Including the other experiments into the optimization of the kinetic parameters could remedy the variation. Another possibility that could have caused these variations is that the chemical mechanism does not contain an important step for the decomposition of the polyurethane foam. For example, reactions 9 and 10 (severing the amine bridge) are treated as irreversible reactions and may be reversible. Other reactions or components may not be included in the mechanism (i.e. the carbonaceous residue found after the decomposition).

Another possibility for the deviation of the model from the data is that the experiments were all modeled with only one grid cell. Incorporating more grid cells into the model would allow for a better description of the flow patterns and diffusion. Furthermore, the residence time for the various decomposition products could be more accurately determined experimentally. The mass and heat transfer effects inside the foam samples could be described better with more grid cells. Finally, additional grid cells in the modeling approach would likely give a better description of the reversible reactions, since the concentration of the reversible gaseous species is higher near the sample.

As the foam decomposes, some of the gaseous products are released on the outside of the foam, while some are released on the inside of the foam. These products released in the inside of the foam need to travel through the pores of the foam structure to be removed from the sample. This adds a little to the residence time for the reversible reactions to take place. Bubble effects were not modeled here, and present a significant modeling challenge.

While developing the model, care was taken to not use any empirical techniques to force the model to match the data. The vapor/liquid equilibrium was treated as simply as possible. Using non-ideal activity coefficients or transient vapor/liquid equilibrium are possible additions to the model that could help the model predictions match the data. Likewise, for the monomers, dimers, etc., the vapor pressure was calculated from an average molecular weight. The range of molecular weight for each oligomer could vary greatly, and so would the vapor pressure. A more complicated estimation of the vapor pressure could be used.

There is some inherent error in the fitted kinetic parameters due to the thermal lag between the measured and sample temperature. The reactions in the polyurethane foam decompositions are very endothermic, and so the sample temperature is lower than the measured temperature. The difference betwee the measured and actual temperature was minimized as much possible, but there would still be at least a small gradient between the gas and the sample. This thermal lag could be accounted for in a more detailed attempt at modeling the foam decomposition. Furthermore, the activation energy could be changed to a distributed activation energy, allowing more flexibility while fitting the kinetic parameters.

Chapter 11. Conclusions and Recommendations

The conclusions from each chapter are summarized in this chapter. The objectives are discussed first. The conclusions based on the data collection and analyses are then presented. The conclusions from the model development and results are shown next. The recommendations for future work are given last.

Completion of Objectives

All of the objectives of this research have been completed. Reliable pyrolysis data for both the polyurethane foam and the Removable Epoxy Foam at atmospheric and high pressure were obtained. A kinetic scheme for the polyurethane foam decomposition was developed, in collaboration with Sandia National Laboratories. A new model called the MTPUF model, which extends the CPD approach to include mass transfer and confinement effects, was also developed.

The decomposition of the polyurethane foam was modeled using the newly formulated MTPUF model. The main task was to exercise the model to ensure that it was working correctly. The modeling results agreed very well with the atmospheric data. The model also correctly predicted the observed trends with variations in heating rate, pressure and confinement, and came close to describing the magnitudes of the shifts. The secondary objective of accurately defining the initial structure of the Removable Epoxy Foam was also completed and is explained in detail in Appendix A.

Data Summary and Conclusions

It was found during the literature search into the data collection procedures that the thermal delay between the sample and the thermocouple could lead to large errors in the fitted kinetic parameters. While collecting the data, care was taken to reduce the thermal delay between the sample and the thermocouple by using helium as the inert atmosphere, and by reducing the mass of the basket. Helium has a high thermal conductivity, and so by using helium as the inert atmosphere, the heat transfer from the gas to the sample is increased. The mass of the basket contributes greatly to the thermal delay of the sample. By reducing the mass of the basket, the energy needed to heat the basket is reduced, and more energy can go to the heating of the sample. Even with these techniques, it is very likely that there is still a temperature difference between the gas and the sample.

The literature search also revealed that a combination of different heating ramp and isothermal conditions leads to a better determination of the kinetic parameters. Several heating ramp and isothermal conditions were used in the data collection. Various pressure and confinement experiments were also conducted. These experiments allowed for the pressure and confinement effects to be observed.

Initial experiments showed that the buoyancy effects during the data collection in the HPTGA were significant. The buoyancy effects were found to be a function of the temperature ramp, pressure, inert atmosphere, and basket style. The buoyancy effects were found to be highly repeatable. Although the change in the inert atmosphere decreased the buoyancy effects, they were still significant and needed to be accounted for to obtain accurate pyrolysis data.

After the rough TGA data were reduced, two checks were conducted to ensure the accuracy of the buoyancy correction and the HPTGA measurements. The first check was to compare the data collected with the HPTGA with data collected using the TGA at Sandia National Laboratories. The data collected on the two different apparatuses agreed very well. The second check was to stop the TGA experiments at an intermediate point and measure the weights on an independent scale. These partial pyrolysis experiments were then compared with the complete pyrolysis experiments. The data from the partial pyrolysis experiments matched the data from the complete pyrolysis experiments very well for all the conditions tested. The pyrolysis data collected on the high pressure thermogravimetric analyzer are very reliable as illustrated by the two data confirmation techniques. These two checks seem to be capable of showing the reliability of the high pressure thermogravimetric analyzer data that have been corrected for buoyancy effects.

During the analysis of the data from the high pressure TGA, it was found that as the heating rate increased, the mass loss curve for the foam shifted to the higher temperatures (i.e. reactions occurred at higher temperatures) as expected. For the polyurethane foam, as the heating rate was increased from 10 to 20°C/min, the mass loss curve shifted 10°C higher. As the heating rate was increased from 20 to 40°C/min, the mass loss curve shifted 5°C higher. For the Removable Epoxy Foam, as the heating rate was increased from 10 to 20°C/min, the mass loss curve shifted 15°C higher. As the heating rate was increased from 20 to 40°C/min, the mass loss curve shifted 10°C higher. It was also found that as the pressure was increased, the mass loss curve shifted to higher temperatures as expected. For the polyurethane foam, a pressure increase from 1 to 10 bars caused the mass loss curve to increase by 10°C. As the pressure was increased to 30 bars, the shift increased to 20°C. With either a pressure of 50 or 70 bars, the mass loss curve increased by 40°C. For the Removable Epoxy Foam, as the pressure was increased from 1 to 10 bars, the mass loss curve shifted 20°C higher. With either a pressure of 30 or 50, the mass loss curve increased by 40°C. Furthermore, it was noted that as the pressure was increased, the carbon dioxide production increased, and the shift in the pyrolysis mechanism for the polyurethane foam observed at atmospheric pressure at 350°C became less apparent.

Modeling Summary and Conclusions

An approach was developed to include the capability for flow in and out of the cell for the polyurethane foam decomposition model. Basically, the modeling approach changed from a batch reactor to a continually-stirred reactor. The general case was designed to describe the flow in and out of both the vapor and condensed phase and would be applicable in a computation fluid dynamics simulation.

The initial structure of the polyurethane foam was first divided into sites, bridges, side chains and light molecules. Using the primary decomposition products as guides, a decomposition mechanism for the polyurethane foam was developed in collaboration with Sandia National Laboratories. The decomposition mechanism generated the majority of the observable decomposition species. The rate equations derived from the chemical mechanism were of the standard Arrenhius form. Populations of species (rather

than concentrations) were used in the rate equations due to their intrinsic nature, and ease of use in the percolation lattice statistics and the population balance theory.

A population balance theory was then derived in this project to allow for the capability of modeling the flow in and out of the cell. The theory was separated into two sections: bridges breaking and bridges forming. The population balance theory uses percolation lattice statistics in conjunction with several newly-developed equations. The percolation lattice statistics were extended to illustrate the cut-off point technique. The cut-off technique is a common numerical practice used while implementing percolation lattice statistics, where large oligomers are assumed to have similar properties as the infinite matrix. A cut-off point (n_{max}) is used to limit the number of oligomers considered in the calculations. The cut-off point used in this research was 6, since that value was found to give results independent of the cut-off point. One of the outcomes from using the cut-off point technique is that the pseudo-p_{crit} drops to zero. An approximate pseudo p_{crit} can be calculated if an approximate zero technique is used. The pseudo- p_{crit} calculated in this research was 0.016. The population balance theory was shown to match the percolation lattice statistics for the non-flow case, as well as for cases with flow. The best accuracy versus computational time was found by using only the 2- and 3-group equations for the bridge forming section, since the probability of four oligomers connecting together and vaporizing was low.

The vapor/liquid equilibrium was based on an isothermal flash calculation using Raoult's law. The compressibility factor was calculated to correct the pressure for nonidealities. The non-ideal behavior was generally important at pressures above 10

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atmospheres. The conversion factors used to change the population variables to masses were then clarified.

The kinetic parameters were fit to the atmospheric data through a simulated annealing algorithm, while forcing the preexponential factor to be dependent on the activation energy. The activation energies for the reactions varied from 22,000 to 64,000 cal/mol, which are in the expected range. With these kinetic parameters, the modeling results matched the atmospheric decomposition data very well. Only minor discrepancies between the data and the modeling results were observed. The resulting model agreed with data from the different heating rate experiments as well as the isothermal experiments. The test of kinetic parameters against a combination of data from both different heating rates and isothermal experiments seems to be capable of generating convincing results.

The MTPUF model was evaluated using data from the high pressure experiments, but using the kinetic parameters determined from the atmospheric pressure experiments. The MTPUF model successfully predicted the trend of increasing reaction temperatures with increasing pressure. Quantitative agreement with the data was acceptable, but could be improved. Furthermore, the MTPUF model correctly predicted the observed increase in the carbon dioxide production at increased pressures, as well as the corresponding decrease in the toluene diisocyanate production. The MTPUF model seems capable of predicting the pressure dependence on the polyurethane foam decomposition from these results.

The MTPUF model was then evaluated using data from the confinement experiments, but using the kinetic parameters determined from the atmospheric pressure

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experiments. The MTPUF model successfully predicted the trend of increasing reaction temperature with decreasing orifice size. Quantitative agreement with the data was acceptable, but could be improved. Furthermore, the MTPUF model correctly predicted the observed increase in the carbon dioxide production at decreased orifice sizes, as well as the corresponding decrease in the toluene diisocyanate production. The MTPUF model seems capable of predicting the confinement effects on the polyurethane foam decomposition from these results.

A limited set of data from totally-confined experiments were modeled using the kinetic parameters determined from the atmospheric pressure experiments as a final exercise for the MTPUF model. The results agreed with the data very well. Both of the predictions showed a 20 minute earlier rise in the piston displacement than observed. The initial pressurization of the gas inside the closed cells could account for this deviation as discussed earlier. This comparison further shows that the MTPUF model seems capable of predicting the confinement effects on the polyurethane foam decomposition.

Recommendations

The decomposition of foam encapsulants has been studied at Sandia National Laboratories and Brigham Young University extensively. The on-going research will probably continue. While great progress in the modeling of the decomposition of the encapsulants has been made in this dissertation, more issues and ideas on how to continually improve the state of the art have arisen. The following are a list of recommendations that could improve the precision and usefulness of the foam decomposition modeling.

- Include the high pressure and confinement experiments in the optimization of the kinetic parameters to get a better fit for those experiments.
- Develop a more detailed chemical decomposition mechanism, to include more of the decomposition products (i.e., the carbonaceous residue remaining at the end of the experiment).
- Model the various experiments in multi-dimensions using mini-grid cells to resolve spatial variations.
- Incorporate and determine the temperature difference between the measured and actual temperature of the sample into the calculations of the kinetic parameters.
- Increase the complexity of the vapor/liquid equilibrium submodel by adding transient behavior or activity coefficients.
- Develop a more complex method for the oligomer vapor pressure, involving the distribution of the molecular weight.
- Use a more complex form of the activation energy by adding a distribution function.

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Appendix A. Determination of Removable Epoxy Foam Structure

The structural units of the Removable Epoxy Foam were determined in this project through analysis of the synthesis method and the starting materials. The process of determining the structure and the results are discussed in detail in the remainder of this section. Figure A.1 shows the most common structural units of the Removable Epoxy Foam that were determined from the analysis.

The structural units show the Removable Epoxy Foam to be a large matrix (essentially infinite) of a polyfunctional acrylate, which was assumed to be similar to pentaerythritol triacrylate (PETA), connected with n-aminoethylpiperazine (n-AEP), nonyl phenol (NP), and dimethyldicyane (DMDC). The DMDC is then connected to diglycidyl ether of bisphenol A (DGEBA) and Removable Epoxy Resin (RER). Mechanisms of decomposition can be developed from these structural units.

The procedure used to determine the initial structure of the Removable Epoxy Foam involved four steps.

- 1. The major ingredients were identified and the molar ratios of the ingredients were calculated.
- 2. The dominant reactive groups were determined along with their respective relative reactivities.



Figure A.1 Most common chemical structural units of Removable Epoxy Foam. The graphic symbols are composed of ingredients used to make the specific foam.

3. The most probable reactions were then postulated and consequently the bonds formed and their distributions were calculated. In addition, a representative monomer unit was generated. This monomer unit was chosen to match the molar ratios of the ingredients, along with the other important quantities, while keeping the total size of the monomer unit to a minimum. 4. A cartoon that contained the above information was generated. Each of these steps will be explained in more detail below.

Assumptions

Many assumptions were made during the determination of the important structural features of the REF and are summarized below. The assumptions will be discussed in further detail below.

- The amount of diethylenetriamine in Epi-Cure 3270 is negligible in the total mixture (> 0.2 wt%).
- 2. The blowing agent and the surfactant do not incorporate into the polymer structure.
- 3. No reaction occurs between the pentaerythritol triacrylate (PETA) and the diglycidyl ether of bisphenol A (DGEBA).
- 4. No small species are generated in the polymerization reactions.
- 5. In Part A, the reactivity of the acrylate groups is higher than the reactivity of the epoxy groups.
- 6. The reactivities of the functional groups in Part B have the following order: NH2
 ~ OH (nonyl phenol) > NH > N ~ OH (PETA).
- 7. The A functionality groups are assumed to all be reacted.

Ingredients

The major ingredients were identified using a combination of Sandia National Laboratory Reports, MSDS's, personal communications and experiments. The major paper containing the formulation of the REF was written by the developers of the REF, Edward M. Russick and Peter B. Rand (Aubert et al., 2001). A table adapted from this paper containing the commercial components of the REF is shown below.

The commercial ingredients are received in two separate parts, RER1 and EPON 8121 (Part A, resins), and Epi-Cure 3270, Ancamine 2049, DC-193, and FC-72 (Part B, curing agents, surfactant, and blowing agent), which are then mixed together when a foam is desired.

Table A.1 Commercial ingredients in KET.							
Commercial Ingredient	Amount	Amount (wt%)	Amount (wt%, w/o DC-193 or FC-72)				
Removable Epoxy Resin (RER1)	60 % of resin	33.90	41.96				
Shell EPON 8121 epoxy resin	40 % of resin	22.60	27.97				
Shell Ancamine 2049 curative	31 parts/hundred resin (phr)	17.51	21.68				
Shell Epi-Cure 3270 curative	12 phr	6.78	8.39				
Air Products DC- 193 (surfactant)	9 phr	5.08	-				
3 M Fluorinert FC- 72 (blowing agent)	25 phr	14.12	-				

Table A.1Commercial Ingredients in REF.

Removable Epoxy Resin

The chemical structure of RER1 was described in detail by Russick and Rand (Aubert et al., 2001) and is shown below in Figure A.2. The letter "R" within a circle will abbreviate the structure of the RER1 molecule in later figures.



® Removable Epoxy Resin 1 (RER1)

Figure A.2 Cartoon of the structure of the RER1.

EPON 8121

The chemical compositions, along with the structures of the major ingredients of EPON 8121, were determined through a combination of the MSDS sheets (Shell Chemicals, 2000c), experimental results and personal communications (Erickson, 2001). The two major components of EPON 8121 are 60 wt% of diglycidyl ether of bisphenol A (DGEBA) and 40 wt% of a polyfunctional acrylate, which was assumed to be similar to pentaerythritol triacrylate (PETA). The structures of these two compounds are shown below in Figure A.3. Similarly, the circled letters "S" and "P" will abbreviate the structures of DGEBA and PETA, respectively in later figures.





© Diglycidyl Ether of Bisphenol A (DGEBA) © Pentaerythritol Triacrylate (PETA) Figure A.3 Cartoon of the structure of the major components of EPON 8121

Epi-Cure 3270 and Ancamine 2049

The chemical compositions, along with the structures of the major ingredients of Epi-Cure 3270 were determined through a combination of the MSDS sheets (Shell Chemicals, 2000b), and personal communications (Erickson, 2001). The three determined major components of Epi-Cure 3270 are < 2 wt% diethylenetriamine (DET), 28 wt% n-aminoethylpiperazine (n-AEP), and 72 wt% nonyl phenol (NP). Since the Epi-Cure 3270 is only 8.39 wt% of the total polymer structure (w/o DC-193 or FC-72 included), the amount of DET in REF is < 0.2 wt% (0.0839 · 0.02) and so was neglected in the determination of the REF chemical structure (assumption 1). The chemical composition of Ancamine 2049 was shown through the MSDS sheets (Shell Chemicals, 2000a) to be ~100% dimethyldicyane (DMDC). The structures of the two major compounds of Epi-Cure 3270, along with the structure of DMDC are shown below in Figure A.4. Similarly, the circled letters "Na", "No" and "T" will abbreviate the structures of n-AEP, NP and DMDC, respectively in later figures.



Figure A.4 Cartoon of the structure of the major components of Epi-Cure 3270 and Ancamine 2049.

DC-193 and FC-72

DC-193 was specified from the MSDS sheets (3M, 2000) to be a polysiloxane, while FC-72 was specified by the MSDS sheets (Air Products, 2000) to be mainly C_6F_{14} . The surfactant and the blowing agent are very non-reactive, but serve as physical regulators of the foam structure and so were assumed to not incorporate into the polymer structure (assumption 2).

Results

With the major components identified, the molar percent in the polymer structure of each component could then be determined. Table A.2 displays the distribution of the major components in the polymer.

Ingredient	Amount	Wt%	Mol%
RER1	60 % of resin	41.96	16.29
DGEBA	24 % of resin	16.78	18.48
PETA	16 % of resin	11.19	14.06
n-AEP	3.36 phr	2.35	6.81
NP	8.64 phr	6.04	10.28
DMDC	31 phr	21.68	34.08

Table A.2Chemical Ingredients in REF.

Reactive Groups

With the major ingredients identified, the reactive groups of each ingredient along with the respective reactions were then determined. The important reactive groups in this system were determined to be the epoxy groups, the acrylate groups, the amine groups and the hydroxyl groups. The acrylate group can react with the epoxy group, but only at high temperatures. Consequently, the PETA, RER1 and the DGEBA in Part A were assumed to not react with each other (assumption 3). The most probable reactions to occur with the four reactive groups described above are shown in Figure A.5. Each of these reactions showed no small species evolving, and so no evolution of small species was assumed (assumption 4).

With the reactive groups identified, the relative reactivities of the different groups were then assumed. For ease of discussion the groups were labeled as A groups for the epoxy groups and the acrylate groups, and B groups for the amine groups and the hydroxyl groups. In the A group, the epoxy groups from the RER1 and the DGEBA were assumed to be equally reactive, but less reactive than the acrylate groups of the PETA (assumption 5). The acrylate groups will be denoted by A(1) groups, while the epoxy groups will be referred to later as the A(2) groups. In the B group, the hydroxyl groups connected to a benzene ring (as in nonyl phenol) and any primary amine groups were assumed to be the most reactive, followed by the secondary amine groups, which will be referred to later as the B(1) groups and B(2) groups, respectively. The hydroxyl groups attached to straight chains and any tertiary amine groups were then assumed to be in the least reactive group (assumption 6). The B(1) and B(2) groups have more reactive groups then the total of the A(1) and A(2) groups (to be shown later). Due to this excess of B groups, the third group was assumed to not react. Also, with such an excess of the B groups, the A groups are assumed to all be reacted (assumption 7).



Figure A.5 Probable reactions between epoxy groups, acrylate groups, hydroxyl groups and amine groups.

Bond Distribution

With these assumptions, the number of bonds between the different A groups and B groups were then calculated using the relative amounts of each ingredient. To do this,

the number of groups contained in each ingredient, along with a comparison of total groups on a 10,000 molecule basis, was proposed as shown below in Table A.3.

	•	# of			Total groups				
		functional groups			(10,000 molecule basis)				
Ingredient	Mol%	A(1)	A(2)	B(1)	B(2)	A(1)	A(2)	B(1)	B(2)
RER1	16.29	0	2	0	0	0	3,258	0	0
DGEBA	18.48	0	2	0	0	0	3,696	0	0
PETA	14.06	3	0	0	0	4,218	0	0	0
n-AEP	6.81	0	0	1	2	0	0	681	1,362
NP	10.28	0	0	1	0	0	0	1,028	0
DMDC	34.08	0	0	2	2	0	0	6,816	6,816
Total	100.00					4,218	6,954	8,525	8,178

Table A.3Number of functional groups in each ingredient, along with a
comparison of total groups on a 10,000 molecule basis.

As seen in Table A.3, for a basis of 10,000 molecules, there are 11,172 (4,218 + 6,954) total A groups, and 16,703 (8,525 + 8,178) total B groups. Since the limiting groups are the A groups, there can be only 11,172 total bonds. These 11,172 bonds would include all of the B(1) groups, and ~32% (2,647 / 8,178) of the B(2) groups. For each bond, two different ingredients are connected together. This means that for the total A component of the bonds, 29.16% (3,258 / 11,172) come from the RER1, while 33.08 (3,696 / 11,172) and 37.76% (4,218 / 11,172) come from the DGEBA and the PETA, respectively. Similarly, for the total B component of the bonds 6.10 (681 / 11,172), 9.20 (1,028 / 11,172), and 61.01% (6,816 / 11,172) come from the nAEP (primary amine group), NP (hydroxyl group), DMDC (primary amine group), respectively. This leaves 2,647 (11,172 - 8,525) of the B component of the bonds 3.95 ((1,362 / 11,172) · (2,647 / 7,1

8,178)), and 19.75% ((6,816 / 11,172) · (2,647 / 8,178)) come from the n-AEP (secondary amine group), and the DMDC (secondary amine group), respectively.

Next, with the overall distribution of the two components of the bond determined, the distribution of the different combinations of the different ingredients can be found. The groups were assumed to react in a sequential order. First the A(1) groups were reacted with the B(1) groups. Since, there are more B(1) groups (8,525) than A(1) groups (4,218), the remaining 4,307 (8,525 – 4,218) B(1) groups were then reacted with the A(2) groups. Also, since there are more B(1) groups than A(1) groups, the A(1) groups statistically could not react with the B(2) groups. The possibility exists, but is not very likely. Since, there are more A(2) groups (6,954) than the remaining B(1) groups (4,307), the remaining 2,647 (6,954 - 4,307) A(2) groups were then reacted with the B(2) groups. The results of reaction scheme are shown below in Table A.4. As seen in Table A.4, no bonds were formed from the PETA and the second reactive group.

	RER1	DGEBA	PETA	Total
n-AEP (1)	1.44%	1.64%	3.02%	6.10%
NP	2.18%	2.47%	4.55%	9.20%
DMDC (1)	14.44%	16.38%	30.19%	61.01%
n-AEP (2)	1.85%	2.10%	0.00%	3.95%
DMDC (2)	9.25%	10.50%	0.00%	19.75%
Total	29.16%	33.08%	37.76%	100.00%

Table A.4Percent of total bonds attributed to the different combinations of the
different reactants.

Representative Monomer Units

The data in Tables A.2 (overall mole percent) and A.4 (bond distribution) can be used to generate a representative monomer unit from the ingredients. To generate a representative monomer unit, the total number of molecules desired in the representative monomer unit was multiplied by the mole percent of the particular ingredient in the overall polymer structure. The results were then rounded to the nearest integer (or half integer if applicable). Half integers were applied to ingredients that had an axis of symmetry. After all of the ingredients were assigned an integer (or half integer) value, the mole percent was then re-calculated on this new basis. The new mole percents were then compared to the overall mole percents. The differences were compared absolutely (by difference) and relatively (percent error). Furthermore, a comparison between the bond percents for the representative monomer unit and the overall polymer structure was made.

As can be expected, as the total number of molecules used to generate the representative monomer unit increased, the absolute and relative error decreased, along with the bond error. On the other hand, as the total number of ingredients increased, the complexity of composing a cartoon of the possible structure increased. For example, to match the above data to four significant figures, a representative monomer unit of 10,000 molecules could be used, but of course the resulting cartoon of how these 10,000 molecules bond together is extremely complex.

Three representative monomer units with varying levels of complexity will be illustrated here. The first monomer unit, formed from 29.5 molecules, was developed to achieve a low absolute, relative and bond error and while maintaining a moderate number of molecules. The second monomer unit, formed from 6 molecules, was developed based on a low number of molecules while maintaining a moderate absolute, relative and bond error. The third monomer unit, formed from 14.5 molecules, was developed as an

intermediate solution between the other two monomer units. A comparison of the calculated mole percent of the three monomer units to the overall polymer structure is shown below in Table A.5.

units and the over an polymer structure.								
	Overall	Large Molecule		Medium	Molecule	Small Molecule		
	Mole %	Number	Mole %	Number	Mole %	Number	Mole %	
RER1	16.29	5.0	16.95	2.5	17.24	1.0	16.67	
DGEBA	18.48	5.5	18.64	2.5	17.24	1.0	16.67	
PETA	14.06	4.0	13.56	2.0	13.79	1.0	16.67	
n-AEP	6.81	2.0	6.78	1.0	6.90	0.5	8.33	
NP	10.28	3.0	10.17	1.5	10.34	0.5	8.33	
DMDC	34.08	10.0	33.90	5.0	34.48	2.0	33.33	
Total	100.00	29.5	100.00	14.5	100.00	6.0	100.00	

Table A.5	Comparison of mole percentages for the three representative monomer
	units and the overall polymer structure.

Table A.6 compares the calculated bond percent of the three monomer units to the overall polymer structure.

units and the overall polymer bildetale.								
		Overall		Large Molecule				
	RER1	DGEBA	PETA	RER1	DGEBA	PETA		
n-AEP (1)	1.44%	1.64%	3.02%	1.52%	1.52%	3.03%		
NP	2.18%	2.47%	4.55%	3.03%	3.03%	3.03%		
DMDC (1)	14.44%	16.38%	30.19%	15.15%	15.15%	30.30%		
n-AEP (2)	1.85%	2.10%	0.00%	1.52%	1.52%	0.00%		
DMDC (2)	9.25%	10.50%	0.00%	9.09%	12.12%	0.00%		
	Me	dium Mole	cule	Small Molecule				
	RER1	DGEBA	PETA	RER1	DGEBA	PETA		
n-AEP (1)	-	3.13%	3.13%	-	-	7.14%		
NP	3.13%	3.13%	3.13%	-	-	7.14%		
DMDC (1)	15.63%	15.63%	31.25%	14.29%	14.29%	28.57%		
n-AEP (2)	3.13%	-	0.00%	-	-	0.00%		
DMDC (2)	9.38%	9.38%	0.00%	14.29%	14.29%	0.00%		

Table A.6Comparison of bond percent for the three representative monomer
units and the overall polymer structure.

(-) represents no bond shown in cartoon.

Due to the low amounts of ingredients in the two smaller monomer units, there are not enough ingredients to generate all of the required bonds. This can be seen by the dashes present in Table A.6. There should be no bonds between the acrylate groups of PETA and the B(2) groups in the monomer unit, and so 0.00% is shown rather than a dash for those bonds.

Cartoons

Cartoons developed from the three representative monomer units, which show possible structures of the polymer, are shown below in Figures A.6, A.7 and A.8. For ease, the condensed notation comprising of the molecule being represented by a letter in a circle was used to generate these cartoons. To reiterate, the circled letters "R", "S", "P", "Na", "No", and "T" represent the structures of RER1, DGEBA, PETA, n-AEP, NP, and DMDC. The structures contained in brackets with the word "or" signify that 50% of the time one of the choices is present (and consequently, 50% of the time the other is present). If a line is drawn were an apparent end of the chain exists, this signifies that only half of the molecule is present in the representation, and the molecule actually continues on. Since there are two sites in the second reactive group for the n-AEP, whenever two bonds are connected to a circled "Na", 50% of the time it represents the second bond attached to the same nitrogen as the primary bond, while 50% of the time, the second bond is attached to the opposite side (see Figure A.4).



Figure A.6 Cartoon of the small molecule (6 molecules).



Figure A.7 Cartoon of the medium molecule (14.5 molecules).



Figure A.8 Cartoon of the large molecule (29.5 molecules).

Summary

To summarize, The procedure used to determine some of the important structural features of the Removable Epoxy Foam (REF) involved four steps.

- 1. The major ingredients were identified and the molar ratios of the ingredients were calculated.
- 2. The dominant reactive groups were determined along with their respective relative reactivities.
- The most probable reactions were postulated and consequently, the bonds formed and their distributions were calculated. In addition, a representative monomer unit was generated.
- 4. A cartoon of the molecule that contained the above information was generated.

The monomer unit was chosen to match the molar ratios of the ingredients, along with the other important quantities, while keeping the total size of the monomer unit to a minimum. The large molecule generated from 29.5 molecules is recommended for use in analysis and determination of decomposition reactions, if it is important that the bond structure need a high amount of detail. The small molecule generated from 6 molecules is recommended if the total size needs to be kept at a minimum, and the bond structure is not as important. The figure at the beginning of this appendix was generated from the 6 molecule representation.

Appendix B. Other Partial Experiments

In this appendix, other results from partial experiments are shown below. The circles indicate the end of the partial experiment.



Figure B.1 Illustration of how the partial experiments compare with the average and limits for an isothermal experiment. (400°C, PUF, He, 1 bar)



Figure B.2 Illustration of how the partial experiments compare with the average and limits for an isothermal experiment. (200°C, REF, He, 1 bar)



Figure B.3 Illustration of how the partial experiments compare with the average and limits for an isothermal experiment. (300°C, REF, He, 1 bar)



Figure B.4 Illustration of how the partial experiments compare with the average and limits for a ramped experiment. (20°C/min, REF, He, 1 bar)

Appendix C. Justification of the Bridge Breaking Population Balance Equations

The derivation of the bridge breaking equations in the population balance theory (Equations 7.10 and 7.11) arose from several discussions with Dr. Bruce Collins (2002). The results of these discussions are presented below. The key to determine the form of C_{nmbr} (or C(n,m,br) as seen in this discussion) is the observation that a complete listing of all possible oligomers that can be generated recursively from the corresponding list for an (n-1)-mer. Since an n-mer has n-1 bridges, there are 2^{n-1} possible sets of fragments (each bridge either breaks or does not break). Of these, there are

$$\binom{n}{0} = 1 \text{ set consisting of a single n-mer,}$$
$$\binom{n}{1} = n \text{ sets consisting of two oligomers: (1,n-1), (2,n-2),..., (n-1,1),}$$
$$\binom{n}{2} = n(n-1)/2 \text{ sets consisting of three oligomers: (1,1,n-2),...,(n-2,1,1), etc.}$$

These 2^{n-1} sets can be obtained from the listing for an (n-1)-mer by the following two steps:

- a) add 1 to the length of the first oligomer in each set, and
- b) append a monomer to the beginning of each set.

For example: $n = 1 \rightarrow (1)$ (monomer cannot decompose further)

 $n = 2 \rightarrow$ step a) produces (2) and step b) produces (1,1)

 $n = 3 \rightarrow$ step a) produces (3) and (2,1) and step b) produces (1,2) and (1,1,1)

 $n = 4 \rightarrow \text{step a}$ produces (4), (3,1), (2,2) and (2,1,1) and step b) produces (1,3), (1,2,1), (1,1,2) and (1,1,1,1)

etc.

Since the length of the list doubles each time step a) and b) are applied, it is clear that the resulting list for an n-mer will contain the required 2^{n-1} sets. Since both steps add 1 to the total lenth of the oligomers in each set, each set in the list for *n* will have a total length of *n*. Since the listing for n = 1 is clearly correct, mathematical induction shows that this procedure will result in the complete and correct list for any value of *n*.

Of course, the entire list does not need to be generated, since the interest is in counting how many ways an n mer can produce an m mer when a specified number of bridges break. Suppose C(n,m,br) is the number of distinct way an m mer can be produced by breaking br in an n-mer, then C(n+1,m,br) can be expressed in terms of C(n,*,*) by tracking the effects of step a) and step b). In the (hypothetical) listing of all sets consisting k fragments of an n-mer, all possible orderings of the fragments are listed. Hence, any m mer in the list will occur equally often in each position (first, second,..., or k^{th}). Adding 1 to the length of the first oligomer in each set removes 1/k of the m mers (converting them to (m+1)-mers) and converts 1/k of the (m-1)-mers (those in the first position) into m mers. Thus, the net effect of step a) on C(n+1,m,br) is to contribute:

$$C(n+1,m,br) = \frac{br}{br+1}C(n,m,br) + \frac{1}{br+1}C(n,m-1,br) + (stepb)$$
(C.1)

Similarly, step b) adds a single monomer to each set so the net effect of step b) on C(n+1,m,br) is to:

$$C(n+1,m,br) = (stepa) + C(n,m,br-1)$$
 (C.2)

for $m = 2, \dots, n - br$, and

$$= (stepa) + C(n, m, br-1) + \binom{n-1}{br-1}$$
(C.3)

for m = 1. Combining Equations C.2 and C.3 gives:

$$C(n+1,m,br) = \frac{br}{br+1}C(n,m,br) + \frac{1}{br+1}C(n,m-1,br) + C(n,m,br-1)$$
(C.4)

for m = 2, ..., n - br, and

$$= \frac{br}{br+1}C(n,m,br) + \frac{1}{br+1}C(n,m-1,br) + C(n,m,br-1) + \binom{n-1}{br-1}$$
(C.5)

for m = 1. Mathematical induction demonstrates that $C(n,m,br) = (br+1)\binom{n-m-1}{br-1}$.

Substituting this expression into the right hand side of Equation C.4 gives:

$$C(n+1,m,br) = \frac{br}{br+1}(br+1)\binom{n-m-1}{br-1} + \frac{1}{br+1}(br+1)\binom{n-m}{br-1} + (br\binom{n-m-1}{br-2})$$
$$= br\binom{n-m-1}{br-1} + \binom{n-m}{br-1} + br\binom{n-m-1}{br-2} = br\left[\binom{n-m-1}{br-1} + \binom{n-m-1}{br-2}\right] + \binom{n-m}{br-1}$$
$$= br\binom{n-m}{br-1} + \binom{n-m}{br-1} = (br+1)\binom{n-m}{br-1}$$
(C.6)

as required. Similarly, substituting $C(n,1,br) = (br+1)\binom{n-2}{br-1}$ into Equation C.5 gives:

$$C(n+1,1,br) = \frac{br}{br+1}C(n,1,br) + C(n,1,br-1) + \binom{n-1}{br-1}$$

= $\frac{br}{br+1}(br+1)\binom{n-2}{br-1} + br\binom{n-2}{br-2} + \binom{n-1}{br-1} = br\left[\binom{n-2}{br-1} + \binom{n-2}{br-2}\right] + \binom{n-1}{br-1}$
= $br\binom{n-1}{br-1} + \binom{n-1}{br-1} = (br+1)\binom{n-1}{br-1}$ (C.7)

as required. For the sake of completion, note that C(n,n,br) = 0, unless br = 0, in which case C(n,n,0) = 1, since if there are zero bridges broken, then only the original size n-mer is possible. Furthermore, when m > n - br, then C(n,m,br) = 0, which comes from the fact that if you break br bridges in an n-mer, then n - br is the maximum size of the oligomer that can be formed in the fragments.

Appendix D. Derivations of the Bridge Forming Population Balance Equations

To reduce the amount of derivations in the main body of the dissertation, the derivation of the other bridge forming population balance equation will be shown in this Appendix. To derive the other population balance equations, first a review of the derivation of the Equation 7.22 will be presented. Then the subsequent derivations will be shown.

Review of 2-group Derivation

An equation for the mole fraction of an n-mer that formed fr bridges as a function of dsc (fraction of side chains that reacted) can be derived from the binomial distribution. The standard binomial distribution form can be applied since there are only two possible outcomes for each side chain, forming a bridge or not. The equation used to calculate the distribution of how many bridges an oligomer formed on a mole fraction basis is:

$$\frac{mol_n^{fr}}{mol_n} = \begin{pmatrix} \mathbf{t}_n \\ fr \end{pmatrix} \cdot (1 - dsc)^{\mathbf{t}_n - fr} \cdot dsc^{fr}$$
(7.17)

This equation has essentially the same form as Equation 2.14 in the percolation lattice statistics and Equation 7.10 in the bridge breaking section of the population balance theory.

Once the quantities of side chains that form bridges are calculated, as outlined above, the population of each oligomer size must be recalculated in a consistent manner. For example, if a monomer attaches to a dimer, the population of monomers and dimers must be decreased and the population of trimers must be increased. The easiest configuration to consider as an example is the 2-group from Figure 7.5. The 2-group represents an i-mer that formed only one connection and connected with a j-mer with only one connection. An equation to calculate the number of moles of a (i+j)-mer generated (mol_{i+j}^{gen}) can be derived from the following procedure. First, the total moles of i-mer (mol_i) , at the beginning of the time step, should be multiplied by the mole fraction

of the i mers that only formed one bridge $(\frac{mol_i^1}{mol_i})$, which comes from Equation 7.17.

Then that product should be multiplied by the probability that the i mer reacted with a jmer that only formed one bridge ($prob_j^1$). This is illustrated below in Equation 7.18:

$$mol_{i+j}^{gen} = mol_i \cdot \frac{mol_i^1}{mol_i} \cdot \frac{prob_j^1}{2}$$
(7.18)

The factor of two in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-3 is different than the set 3-1).

The probability $(prob_j^1)$ is defined as the ratio of the number of reacted side chains on the j-mer (tot_j^{fr}) to the total number of reacted side chains (tot_j^{fr}) :

$$prob_n^{fr} = \frac{tot_n^{fr}}{tot^{fr}}$$
(7.19)

The total number of reacted side chains on an n-mer with fr reacted side chains is simply fr multiplied by the moles of n-mer (mol_n) , and then multiplied by the mole fraction of the n-mer with fr reacted side chains (Equation 7.17), and is shown below in Equation 7.20.

$$tot_n^{fr} = \begin{pmatrix} \boldsymbol{t}_n \\ fr \end{pmatrix} \cdot (1 - dsc)^{\boldsymbol{t}_n - fr} \cdot dsc^{fr} \cdot fr \cdot mol_n$$
(7.20)

The total number of side chains that reacted can be calculated by summing the moles of side chains attached to the oligomers and the moles of side chains attached to the infinite matrix (sch_{inf}):

$$tot^{fr} = \left(\sum_{n=1}^{n \max} \boldsymbol{t}_n \cdot mol_n + sch_{\inf}\right) \cdot dsc$$
(7.21)

which is the same as calculating the total number of side chains and then multiplying by the percent decrease of side chains. Substituting Equations 7.17, 7.19-7.21 into Equation 7.18 and combining terms gives the equation for the mole generation of a (i+j)-mer (process D in Figure 7.4) for 2-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j}^{gen} = \frac{1 \cdot \begin{pmatrix} \boldsymbol{t}_{j} \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_{j} \\ 1 \end{pmatrix} \cdot (1 - dsc)^{\boldsymbol{t}_{i} + \boldsymbol{t}_{j} - 2} \cdot dsc^{2} \cdot mol_{i} \cdot mol_{j}}{2 \cdot tot^{fr}}$$
(7.22)

Now, when calculating the mole generation of a (i+j)-mer, there are n_{max}^2 possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 2-3 is a mirror image of 3-2). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max}) -mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-1, 2-2, etc.) These terms do not have a mirror image term, and so the factor of two in the denominator in Equation 7.19 and 7.22 should remain.

3-group Derivation

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner for the 3-group (as shown in Figure 7.5). The 3-group represents an i-mer that formed two connections and connected with a j-mer and a k-mer each with only one connection. An equation to calculate the number of moles of an (i+j+k)-mer generated (mol_{i+j+k}^{gen}) can be derived from the following procedure. First, the total moles of i-mer (mol_i) , at the beginning of the time step, should be multiplied by the mole fraction of the i-mers that formed two bridges $(\frac{mol_i^2}{mol_i})$, which comes from Equation 7.17. Then that product should be multiplied by the probability that the i-mer reacted with a j-mer that only formed one bridge $(prob_i^1)$. Then that product should be multiplied by the probability that the only formed one bridge $(prob_i^1)$. Then that only formed one bridge $(prob_i^1)$.

$$mol_{i+j+k}^{gen} = mol_i \cdot \frac{mol_i^2}{mol_i} \cdot \frac{prob_j^1 \cdot prob_k^1}{2}$$
(D.1)

The factor of two in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-1-3 is different than the set 3-1-1). Substituting Equations 7.17, 7.19-7.21 into Equation D.1 and combining terms gives the equation for the mole generation of a (i+j+k)-mer (process D in Figure 7.4) for 3-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j+k}^{gen} = \frac{2 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijk-4} \cdot dsc^4 \cdot mol_{i-k}}{2 \cdot (tot^{fr})^2}$$
(7.23)

where

$$tijk = t_i + t_j + t_k \tag{7.29}$$

$$mol_{i-k} = mol_i \cdot mol_j \cdot mol_k \tag{7.30}$$

the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5. Now, when calculating the mole generation of a (i+j+k)-mer, there are n_{max}^{3} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 1-2-3 is a mirror image of 3-2-1). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max}) -mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-3-1, 2-1-2, etc.) These terms do not have a mirror image term, and so the factor of two in the denominator in Equation D.1 and 7.23 should remain.

4a-group Derivation

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner for the 4a-group (as shown in Figure 7.5). The 4a-group represents an i-mer that formed two connections and connected with a j-mer that formed two connections, which then connected with a k-mer and an 1-mer each with only one connection. An equation to calculate the number of moles of a (i+j+k+1)-mer generated $(mol_{i+j+k+1}^{gen})$ can be derived from the following procedure. First, the total moles of i-mer (mol_i) , at the beginning of the time step, should be multiplied by the mole fraction of the i-mers that formed two bridges $(\frac{mol_i^2}{mol_i})$, which comes from Equation 7.17. Then that product should be multiplied by the probability that the i-mer reacted with a j-mer that formed two bridges $(prob_j^2)$. Then that product should be multiplied by the probability that the probability the probabil

that the (i+j)-mer reacted with a k-mer that only formed one bridge ($prob_k^1$). Finally, the product should then be multiplied by the probability that the (i+j+k)-mer reacted with an l-mer that only formed one bridge ($prob_l^1$). This is illustrated below in Equation D.2:

$$mol_{i+j+k+l}^{gen} = mol_i \cdot \frac{mol_i^2}{mol_i} \cdot \frac{prob_j^2 \cdot prob_k^1 \cdot prob_l^1}{4}$$
(D.2)

The factor of four in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-1-1-3 is different than the set 3-1-1-1), and there are two sets of symmetric pairs in the representation (i.e., i and j; k and l). Substituting Equations 7.17, 7.19-7.21 into Equation D.2 and combining terms gives the equation for the mole generation of a (i+j+k+l)-mer (process D in Figure 7.4) for 4a-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j+k+l}^{gen} = \frac{4 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot \begin{pmatrix} 1 - dsc \end{pmatrix}^{tijkl-6} \cdot dsc^6 \cdot mol_{i-l}}{4 \cdot (tot^{fr})^3}$$
(7.24)

where

$$tijkl = t_i + t_j + t_k + t_l \tag{7.31}$$

$$mol_{i-l} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l \tag{7.32}$$

the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5. Now, when calculating the mole generation of a (i+j+k+l)-mer, there are n_{max}^{4} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 1-1-2-3 is a mirror image of 3-2-1-1). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max})-mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Some terms have three mirror images (e.g., 1-2-2-1), and need to be multiplied by four to account for the other terms. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-3-2-1, 2-1-2-2, etc.) These terms do not have a mirror image term, and so the factor of four in the denominator in Equation D.2 and 7.24 should remain.

4b-group Derivation

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner for the 4b-group (as shown in Figure 7.5). The 4b-group represents an i-mer that formed three connections and connected with a j-mer, a k-mer and an I-mer each with only one connection. An equation to calculate the number of moles of a (i+j+k+l)-mer generated ($mol_{i+j+k+l}^{gen}$) can be derived from the following procedure. First, the total moles of i-mer (mol_i), at the beginning of the time step, should

be multiplied by the mole fraction of the i-mers that formed three bridges $(\frac{mol_i^3}{mol_i})$, which comes from Equation 7.17. Then that product should be multiplied by the probability that the i-mer reacted with a j-mer that formed only one bridge $(prob_j^1)$. Then that product should be multiplied by the probability that the (i+j)-mer reacted with a k-mer that only formed one bridge $(prob_i^1)$. Finally, the product should then be multiplied by

the probability that the (i+j+k)-mer reacted with an 1 mer that only formed one bridge $(prob_l^1)$. This is illustrated below in Equation D.3:

$$mol_{i+j+k+l}^{gen} = mol_i \cdot \frac{mol_i^3}{mol_i} \cdot \frac{prob_j^1 \cdot prob_k^1 \cdot prob_l^1}{6}$$
(D.3)

The factor of six in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-1-1-3 is different than the set 1-3-1-1), and since the symmetric set contains three oligomers, the denominator is 3! or 6. Substituting Equations 7.17, 7.19-7.21 into Equation D.3 and combining terms gives the equation for the mole generation of a (i+j+k+l)-mer (process D in Figure 7.4) for 4b-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j+k+l}^{gen} = \frac{3 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 3 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot \begin{pmatrix} 1 - dsc \end{pmatrix}^{tijkl-6} \cdot dsc^6 \cdot mol_{i-l}}{6 \cdot (tot^{fr})^3}$$
(7.25)

where

$$tijkl = t_i + t_j + t_k + t_l \tag{7.31}$$

$$mol_{i-l} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l \tag{7.32}$$

the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5. Now, when calculating the mole generation of a (i+j+k+l)-mer, there are n_{max}^{4} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 1-1-2-3 is a mirror image of 1-3-2-1). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max})-mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Some terms have two mirror images (e.g., 1-2-2-2), and need to be multiplied by six to account for the other terms. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-3-3-3, 2-1-1-1, etc.) These terms do not have a mirror image term, and so the factor of six in the denominator in Equation D.3 and 7.25 should remain.

5a-group Derivation

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner for the 5a-group (as shown in Figure 7.5). The 5a-group represents an i-mer that formed two connections and connected with a j-mer that formed two connections and connected with a k-mer that formed two connections and connected with an I-mer and an m-mer each with only one connection. An equation to calculate the number of moles of a (i+j+k+l+m)-mer generated ($mol_{i+j+k+l+m}^{gen}$) can be derived from the following procedure. First, the total moles of i-mer (mol_i), at the beginning of the time step, should be multiplied by the mole fraction of the i-mers that formed two bridges ($\frac{mol_i^2}{mol_i}$), which comes from Equation 7.17. Then that product should be multiplied by the

probability that the i mer reacted with a j-mer that formed two bridges $(prob_j^2)$. Then that product should be multiplied by the probability that the (i+j)-mer reacted with a kmer that formed two bridges $(prob_k^2)$. Next, the product should then be multiplied by the probability that the (i+j+k)-mer reacted with an l-mer that only formed one bridge $(prob_l^1)$. Finally, the product should then be multiplied by the probability that the (i+j+k+1)-mer reacted with an mer that only formed one bridge $(prob_m^1)$. This is illustrated below in Equation D.4:
$$mol_{i+j+k+l+m}^{gen} = mol_i \cdot \frac{mol_i^2}{mol_i} \cdot \frac{prob_j^2 \cdot prob_k^2 \cdot prob_l^1 \cdot prob_m^1}{12}$$
(D.4)

The factor of 12 in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-1-1-1-3 is different than the set 1-1-3-1-1), and since one of the symmetric sets contains three oligomers, and the other symmetric set contain two oligomers, the denominator is 3!2! or 12. Substituting Equations 7.17, 7.19-7.21 into Equation D.4 and combining terms gives the equation for the mole generation of a (i+j+k+l+m)-mer (process D in Figure 7.4) for 5a-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j+k+l+m}^{gen} = \frac{8 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_m \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijklm-8} \cdot dsc^8 \cdot mol_{i-m}}{12 \cdot (tot^{fr})^4}$$
(7.26)

where

$$tijkl = t_i + t_j + t_k + t_l$$
(7.33)

$$mol_{i-l} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l \tag{7.34}$$

the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5. Now, when calculating the mole generation of a (i+j+k+l+m)-mer, there are n_{max}^{5} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 1-1-2-3-1 is a mirror image of 1-3-2-1-1). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max}) -mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Some terms have two mirror images (e.g., 1-2-2-2-2), and need to be multiplied by six to account for the other terms. Furthermore, some of the mirror image terms that are calculated would be completely symmetric (e.g. 1-3-3-3-1, 2-1-1-1-2, etc.) These terms do not have a mirror image term, and so the factor of 12 in the denominator in Equation D.4 and 7.26 should remain.

5b-group Derivation

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner for the 5b-group (as shown in Figure 7.5). The 5b-group represents an i-mer that formed three connections and connected with a j-mer that formed two connections and connected with a k-mer, an I-mer and an m-mer each with only one connection. An equation to calculate the number of moles of a (i+j+k+l+m)-mer generated $(mol_{i+j+k+l+m})$ can be derived from the following procedure. First, the total moles of i-mer (mol_i) , at the beginning of the time step, should be multiplied by the mole

fraction of the i mers that formed three bridges $(\frac{mol_i^3}{mol_i})$, which comes from Equation

7.17. Then that product should be multiplied by the probability that the i mer reacted with a j-mer that formed two bridges $(prob_j^2)$. Then that product should be multiplied by the probability that the (i+j)-mer reacted with a k-mer that formed only one bridge $(prob_k^1)$. Next, the product should then be multiplied by the probability that the (i+j+k)-mer reacted with an i mer that only formed one bridge $(prob_l^1)$. Finally, the product

should then be multiplied by the probability that the (i+j+k+1)-mer reacted with an mer that only formed one bridge ($prob_m^1$). This is illustrated below in Equation D.5:

$$mol_{i+j+k+l+m}^{gen} = mol_i \cdot \frac{mol_i^3}{mol_i} \cdot \frac{prob_j^2 \cdot prob_k^1 \cdot prob_l^1 \cdot prob_m^1}{6}$$
(D.5)

The factor of six in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-1-1-1-3 is different than the set 1-1-3-1-1), and since one of the symmetric sets contains three oligomers, the denominator is 3! or 6. Substituting Equations 7.17, 7.19-7.21 into Equation D.5 and combining terms gives the equation for the mole generation of a (i+j+k+l+m)-mer (process D in Figure 7.4) for 5b-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j+k+l+m}^{gen} = \frac{6 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 3 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 2 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_m \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijklm-8} \cdot dsc^8 \cdot mol_{i-m}}{6 \cdot (tot^{fr})^4}$$
(7.27)

where

$$\boldsymbol{t}ijkl = \boldsymbol{t}_i + \boldsymbol{t}_j + \boldsymbol{t}_k + \boldsymbol{t}_l \tag{7.33}$$

$$mol_{i-l} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l$$
 (7.34)

the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5. Now, when calculating the mole generation of a (i+j+k+l+m)-mer, there are n_{max}^{5} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 1-1-2-3-1 is a mirror image of 1-3-2-1-1). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max}) -mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Some terms have two mirror images (e.g., 1-2-2-2-2), and need to be multiplied by six to account for the other terms. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-3-3-3-1, 2-1-1-1-2, etc.) These terms do not have a mirror image term, and so the factor of six in the denominator in Equation D.5 and 7.27 should remain.

5c-group Derivation

The previous derivation for the bridge forming reactions for the 2-group can be applied in a similar manner for the 5b-group (as shown in Figure 7.5). The 5c-group represents an i-mer that formed four connections and connected with a j-mer, a k-mer, an I-mer and an m-mer each with only one connection. An equation to calculate the number of moles of a (i+j+k+l+m)-mer generated $(mol_{i+j+k+l+m})$ can be derived from the following procedure. First, the total moles of i-mer (mol_i) , at the beginning of the time step, should be multiplied by the mole fraction of the i-mers that formed four bridges $(\frac{mol_i^4}{mol_i})$, which comes from Equation 7.17. Then that product should be multiplied by the probability that the i-mer reacted with a j-mer that formed only one bridge $(prob_j^1)$. Then that product should be multiplied by the probability that the (i+j)-mer reacted with a j-mer that formed only one bridge $(prob_j^1)$.

k-mer that formed only one bridge $(prob_k^1)$. Next, the product should then be multiplied by the probability that the (i+j+k)-mer reacted with an 1-mer that only formed one bridge $(prob_l^1)$. Finally, the product should then be multiplied by the probability that the (i+j+k+1)-mer reacted with an mer that only formed one bridge $(prob_m^1)$. This is illustrated below in Equation D.6:

$$mol_{i+j+k+l+m}^{gen} = mol_i \cdot \frac{mol_i^4}{mol_i} \cdot \frac{prob_j^1 \cdot prob_k^1 \cdot prob_l^1 \cdot prob_m^1}{24}$$
(D.6)

The factor of 24 in the denominator is present, since the order in which the oligomers attach is significant in the calculation scheme (i.e. the set 1-1-1-1-3 is different than the set 1-1-3-1-1), and since one of the symmetric sets contains four oligomers, the denominator is 4! or 24. Substituting Equations 7.17, 7.19-7.21 into Equation D.6 and combining terms gives the equation for the mole generation of a (i+j+k+l+m)-mer (process D in Figure 7.4) for 5c-group as labeled in Figure 7.5, and can be seen below:

$$mol_{i+j+k+l+m}^{gen} = \frac{4 \cdot \begin{pmatrix} \boldsymbol{t}_i \\ 4 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_j \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_k \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_l \\ 1 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{t}_m \\ 1 \end{pmatrix} \cdot (1 - dsc)^{tijklm-8} \cdot dsc^8 \cdot mol_{i-m}}{24 \cdot (tot^{fr})^4}$$
(7.28)

where

$$tijkl = t_i + t_j + t_k + t_l$$
(7.33)

$$mol_{i-l} = mol_i \cdot mol_j \cdot mol_k \cdot mol_l \tag{7.34}$$

the labels of the different oligomer sizes correspond to the labeling shown in Figure 7.5. Now, when calculating the mole generation of a (i+j+k+l+m)-mer, there are n_{max}^{5} possibilities. Of these possibilities many are merely reflections of another possibility (e.g. 1-1-2-3-1 is a mirror image of 1-3-2-1-1). Furthermore, many of the possibilities generate oligomers that are larger than an (n_{max}) -mer, which are then just associated with the infinite matrix. A computationally efficient manner that eliminates the calculation of these unnecessary terms would involve structuring the computation summation loops in such a manner as to eliminate the calculation of the mirror image terms, as well as the larger oligomers. If only one of the mirror image terms is calculated, then the result must be multiplied by two to account for the other term. Some terms have two mirror images (e.g., 1-1-2-2-2), and need to be multiplied by six to account for the other terms. Furthermore, some of the mirror image terms that are calculated would be symmetric (e.g. 1-3-3-3-3, 2-1-1-1, etc.) These terms do not have a mirror image term, and so the factor of 24 in the denominator in Equation D.6 and 7.28 should remain.

Appendix E. Other Evaluations of Population Balance Theory

In this appendix, the other evaluations of the bridge forming section of the population balance theory are shown below.



Figure E.1 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 2-mers. (Bridge forming, s+1=3)



Figure E.2 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 3-mers. (Bridge forming, s+1=3)



Figure E.3 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 4-mers. (Bridge forming, s+1=3)



Figure E.4 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 6-mers. (Bridge forming, s+1=3)



Figure E.5 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 7-mers. (Bridge forming, s+1=3)



Figure E.6 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 8-mers. (Bridge forming, s+1=3)



Figure E.7 Comparison of the relative error versus # of intermediate steps, as well as groups included into the calculation for the 9-mers. (Bridge forming, s+1=3)

Appendix F. Source Code for MTPUF Model

In this appendix the source code for the MTPUF model is shown. The source code was modified to work as a subroutine for the source code of the simulated annealing technique. Only the main program ("mtpuf.f") and the "init.f" subroutines were then modified to give "mtpuf2.f" and "init2.f". The source code was then modified to model the totally confined experiments. The only subroutines that were modified were the main program ("mtpuf.f"), "init.f" and "flow.f" to give "mtpuf3.f", "init3.f" and "flow3.f". Only the modified subroutines are shown in the later sections to eliminate unneeded repetitions.

MTPUF Model

mtpuf.f

```
program mtpuf
C23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x12
C-----C
C The Mass Transfer PolyUrethane Foam (MTPUF) decomposition model is an
С
  extended version of the CPUF model referenced in
С
 (1) Hobbs, M. L., Erickson, K. E., and Chu, T. Y., "Modeling Decomposition
С
С
      of Unconfined Rigid Polyurethane Foam," Polymer Degradation and
      Stability, (1999).
С
С
C The primary difference in the PUF model and the CPUF model is
C the kinetic scheme. The PUF mechanism is based on a retrograde
C reaction followed by the formation of a secondary polymer
C which is stable below about 350 C. This mechanism can be considered a
C generalization of the CPD model developed by Fletcher et al.:
С
                       /--> C1 + G1
C 11 "species"
```

```
С
   9 reactions
                 L* - /--> G2
С
                    \<--> d*-- /--> C2 + G4
                             \--> 2L --
С
С
                              -G3
                                       \<--> d --> G5
С
С
 The MTPUF model is based on Erickson et al. experiments and considers
С
 four different bridge types, 6 side chain types, 4 light molecule types,
С
  and two sites types:
С
C L1 [=] urethane bridge
                              D1 [=] isocyanate side chain
C L2 [=] aminourethane bridge
                             D2 [=] OH side chain
                             D3 [=] aminourethane side chain
C L3 [=] diamine bridge
C L4 [=] adipate bridge
                             D4 [=] diamine side chain
                             D5 [=] CH2 radical side chain
C
C TDI [=] toluene diisocyanate
                             D6 [=] CH2O radical side chain
C TDA [=] toluene diamine
C CPN [=] cyclopentanone
                             S1 [=] TMP site
C CO2 [=] carbon dioxide
                             S2 [=] DEG site
С
С
                    (1\2)
                               (3\4)
C 16 "species"
                  L1 <--> D1 + D2 <--> TDI + 2 D2
                    \(5) (6\7)
\--> L2 <--> D2 + D3
C 11 reactions
С
С
                     -C02
                          (8) (9)
                                           (10)
                            \--> L3 --> D4 + D5 --> TDA + 2 D5
С
С
                            -CO2
С
                   (11)
С
                 L4 --> D5 + CPN + CO2 + D6
С
C y(1) = L1 ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
C y(5) = D1 ; y(6) = D2 ; y(7) = D3 ; y(8) = D4
C y(9) = D5 ; y(10) = D6 ; y(11) = S1 ; y(12) = S2
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
С
C The initial polymer structure is assumed to be composed of two
C bridge types (the urethane and adipate bridges) and two different
C site types (the trimethylol propane, and diethyleneqlycol).
C-----C
implicit double precision (a-h,o-z)
     parameter (neq1 = 16, neq2 = 12, maxt = 4000)
     parameter (lrw = 250+neq1*(10+neq1), liw = 56+neq1)
     dimension rwork(lrw),iwork(liw),info(15)
     double precision L10,L20,L30,L40,lsys0,mw,mwinf,mwinert,mp0
     double precision ms0,ml0,mg0,mtot,mwv,mwf,ms,ml,mg,mi
     double precision y(neq1),yold(neq1)
     double precision w(neq2),ft(neq2),mt(neq2),ywt(neq2),twout(neq2)
     external func
     external rpcrit
common /cdbl1/ CO20,CPN0,D10,D20,D30,D40,D50,D60,S10,S20,TD10,TDA0
     common /cdbl2/ L10,L20,L30,L40
     common /cdbl3/ mw(neq1),mwinf,mwinert
     common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
     common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
     common /cdbl7/ mp0,Vol,conf,fli,fac
     common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,hbas
     common /cint1/ iprint,ntmax
     common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
     common /cttime/ tim(maxt),tem(maxt),timax,ntim
data zero, one, two /0.D0, 1.D0, 2.D0/
     data half, small /0.5D0, 1.D-20/
```

c...[Rq] = cm3*atm/mol/K data Rg /82.057841D0/ C-----C C Call init to initialize parameters and read input files С-----С call init C-----C Initialize solver variables С C------C call sinit(info,atol,rtol) С-----С C Calculate initial values C-----C fmas = one C-----C C y(1) = L1 ; y(2) = L2 ; y(3) = L3 ; y(4) = L4C y(5) = D1 ; y(6) = D2 ; y(7) = D3 ; y(8) = D4C y(9) = D5 ; y(10) = D6 ; y(11) = S1 ; y(12) = S2C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2C-------C _____ y(1) = L10y(2) = L20y(3) = L30y(4) = L40y(5) = D10y(6) = D20y(7) = D30y(8) = D40y(9) = D50y(10) = D60y(11) = S10y(12) = S20y(13) = TDI0y(14) = TDA0y(15) = CPN0y(16) = CO20psys0 = L10+L20+L30+L40psys = psys0lsys0 = CO20+CPN0+TDA0+TDI0 С-----С C Calculate p critical C-----C p0 = zerop1 = siginv call zeroin(rpcrit,p0,p1,rez,aez,iflag) pcrit = p0С-----С C Percolation lattice statistics of initial conditions C-----C call mwavg(y,fsit,fbrg,fsch,flm) call perk(y,psys0,ft,mt,ftinf,totmas) totmasp = totmas+sigp12*flm*lsys0 C-----C C Add the molecular weight of the gases, infinite matrix and inert C-----C do 25 i = 1,ngas 25 mt(i+nmer) = mw(ncom+i) mt(ntot2-1) = mwinfmt(ntot2) = mwinert C-----C C Calculate the masses of the mers and the infinite matrix С-----С

do 50 i = 1, nmer

```
50
     w(i) = ft(i)*mp0*totmas/totmasp
   w(ntot2-1) = ftinf*mp0*totmas/totmasp
C-----C
C Calculate the masses of the light molecules from the initial populations
С-----С
    fac = sigp12*mp0/totmasp
    do 75 i = 1,ngas
75
    w(i+nmer) = y(ncom+i)*mt(i+nmer)*fac
C-----C
C Calculate the amount of inert gas to be added to get
C the correct pressure
С-----С
    count = zero
    vs0 = mp0/rhos
    vq0 = Vol-vs0
    tp0 = tfun(zero,ntim,tim,tem)
C Guess all gas is inert
    w(ntot2) = press*vg0/Rg/tp0*mt(ntot2)
90
    call phases(w,mt,tp0,press,mg0,ml0,ms0,mwv,vg0,comp,ywt)
   press1 = mg0*rg*tp0*comp/vg0/mwv
C-----C
C Check to see if the pressure matches with relative error test (1%)
C-----C
    rperror = (press1-press)/press
    if (abs(rperror) .ge. 0.0001 .and. count .le. 100.D0) then
      w(ntot2) = w(ntot2)*(one-rperror)
      count = count+one
      goto 90
    end if
    do 95 i = 1,ntot2
95
    twout(i) = zero
C-----C
C Begin solvers Do loop
С-----С
   time = zero
    tout = zero
   do 100 iii = 1,ntmax
C-----C
C Call DDEBDF y(1) = L1; y(2) = L2; y(3) = L3; y(4) = L4
C to integrate: y(5) = D1; y(6) = D2; y(7) = D3; y(8) = D4
           y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
С
С
           y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
C-----C
      do 150 i = 1, neq1
        yold(i) = y(i)
150
      if (fmas .lt. 0.0001) then
        time = time+dt
        goto 200
      end if
      tout = time+dt
300
      call ddebdf (func,neq1,time,y,tout,info,rtol,atol,idid,
               rwork,lrw,iwork,liw,rpar,ipar,jac)
200
      tp = tfun(time,ntim,tim,tem)
      info(1) = 0
      if (idid.lt.0) then
        call error (idid,'cpuf.f',1,rwork,info)
      end if
      do 250 i = 1, neg1
250
        y(i) = max(y(i), zero)
C-----C
C Calculate mass (mas) and molecular weight (mt) of gas species and mers
С-----С
```

```
call popmas(y,yold,psys,w,mt)
```

```
C-----C
C Calculate flow effects (with flash included)
С------С
       call flow(y,w,mt,tp,ms,ml,mg,mi,psys,twout)
       fmas = (ms+ml+mg-mi)/mp0
       totm = mg+ms+ml
       if (mod(iii,iprint).eq.0) then
         write(21,1000)time/60.,(y(k),k=1,nreac),psys
         write(22,2000)time/60.,(twout(k),k=1,ntot2)
         write(26,3000)time/60.,tp-273.15,press,fmas,ms,ml,mg,mi,totm
       end if
100
    continue
    close (21)
    close (22)
    close (26)
1000 format(2x, f6.2, 2x, 17(1x, f7.5))
2000 format(2x, f6.2, 2x, 12(1x, e10.3))
3000 format(2x, f6.2, 3x, f6.2, 2x, 7(1x, f8.5))
    end
```

mtpuf.in

6 !nsay..(say(i),i=1,nsay) follows: C-----C Confined PolyUrethane Foam (CPUF) decomposition model C С Sample:TestSize:5.000 mgComment:20 K/minPurge:100 CC He/sec С С С С Operator: Pressure: 1 bar С С-----С 2.8 \$ sig+1 average coordination number 4 0.78 236. \$ L1 mw(1) init. urethane bridge pop. and mw 0. 192. \$ L2 mw(2) init. amino ure. bridge pop. and mw 0. 148. \$ L3 mw(3) init. diamine bridge pop. and mw 0.22 172. \$ L4 mw(4) init. adipate bridge pop. and mw 6 0. 205. \$ D1 mw(5) init. isocyanate side chain pop. and mw 0. 31. \$ D2 mw(6) init. amino urethane side chain pop. and mw 0. 161. \$ D3 mw(7) init. adipate side chain population and mw mw(8) init. diamine side chain pop. and mw
mw(9) init. CH2 radical side chain pop. and mw 134. \$ D4 14. \$ D5 0. 0. 30. \$ D6 0. mw(10) init. CH2O radical side chain population and mw 2 0.78 41. \$ S10 mw(11) site wt. frc. TMP, and mw (ave. site mw = 41.7) 0.22 44. \$ S20 mw(12) site wt. frc. DEG, and mw (ave. site mw = 41.7) 4 0. 174. \$ tdi0 mw(11) init. TDI pop. and mw 0. 120. \$ tda0 mw(11) init. TDA pop. and mw 0. 84. \$ cpn0 mw(12) init. CPN pop. and mw 0. 44. \$ co20 mw(13) init. CO2 pop. and mw 6 8000.\$mw(19) assumed mw of inf. polymer1.755D-64.\$ flimw(20) flowrate and mw of inert gas, cc/sec, g/mol0.0050.353\$ ms0 rhosinit. solid mass and density 0. \$ Vol conf volume in interest, confinement .15 1.31.0 \$ gamma pambratio of specific heats and ambient pressure0.81. \$ dorf corforifice diameter and coefficient0.008\$ hbasbasket height 8.1548E+14 4.0064E+14 2.0500E+14 1.6863E+11 \$ a(1:4) prefactors, 1/s 1.5073E+11 1.5766E+08 9.0602E+10 2.6897E+10 \$ a(5:8) prefactors, 1/s \$ a(9:11) prefactors, 1/s 1.3813E+08 1.1052E+10 7.9114E+16

\$ e(1:4) 42869. 36550. 38948. 29882. act. Energies, cal/mol 37399. 31899. 21959. 35470. \$ e(5:8) act. Energies, cal/mol 30786. 37433. 63458 \$ e(9:11) act. Energies, cal/mol 0. \$ esiq standard dev., cal/mol 1.0 \$ press pressure, atm 725. 30.0 .433782 $\$ Tc (K), Pc (atm), omega for TDI $804.\ 43.2$.579439 \$ Tc (K), Pc (atm), omega for TDA 625. 45.4 .287647 \$ Tc (K), Pc (atm), omega for CPN 304. 72.9 .223621 \$ Tc (K), Pc (atm), omega for CO2 \$ Tc (K), Pc (atm), omega for 1-mer 800. 46.0 .4 800. 46.0 .4 \$ Tc (K), Pc (atm), omega for 2-mer 800. 46.0 .4 \$ Tc (K), Pc (atm), omega for 3-mer and up \$ Tc (K), Pc (atm), omega for infinite 800. 46.0 .4 5.2 2.25 -0.3903 \$ Tc (K), Pc (atm), omega for inert 1.0 10 500. \$ dt0,iprint,dtmax time step, s; print inc.; max dt, s 1800. \$ timax final time in calculation, s 3 \$ ntim number of time points 333.15 0. 120. 333.15 1800. 873.15

error.f

subroutine error (idid, routin, kmon, wkk, info) C-----C C This subroutine outputs error messages for ddebdf c input description c -----_____ -----C c idid error flag for ddebdf С c routin name of the calling routine С c kmon screen monitor switch to output error/warning messages C C-----C implicit double precision (a-h,o-z), integer (i-n) dimension wkk(*), info(*) character routin*(*) C None C None _____c C----c write error messages for ddebdf c-----c if(kmon .eq. 1) then С write(6,110) routin,idid if (idid .eq. 3) then write(6,120) elseif (idid .eq. 2) then write(6,130) elseif (idid .eq. 1) then write(6,140) elseif (idid .eq. -1) then info(1) = 1write(6,150) С elseif (idid .eq. -2) then info(1) = 1С write(6,160) С write(6,165) wkk(12) elseif (idid .eq. -3) then info(1) = 1write(6,170) С

```
elseif (idid .eq. -6) then
          write(6,180)
        elseif (idid .eq. -7) then
          write(6,190)
        elseif (idid .eq. -33) then
          write(6,200)
        else
          write(6,210)
        endif
        if(idid.lt. -5) then
          write(6,220)
          stop
       endif
     endif
    return
C-----
               ______
c 1 2 3 4 5 6 7 c
c23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x1c
c-----c
                            formats
С
                                                               С
G------G
110 format(/,
    1t2,'***** Warning in DEBDF called from ',a, T55,'*****',/,
    1t2, '***** flag = ', i6, '
                                                         *****')
120
   format(
    1t2, '***** The integration to tout was successfully
                                                       *****',/,
    2t2, '***** completed by stepping past tout. The solution *****', /,
                                                         *****')
    2t2, '***** was obtained by interpolation.
130
   format(
    1t2, '***** The integration was successfully completed
                                                        *****',/,
                                                        ****')
    2t2, '***** by stepping exactly to tout.
140
    format(
    1t2, '***** Step successfully taken in the intermediate
                                                        ****',/,
    2t2, '***** output mode. Code has not yet reached tout.
                                                        ****')
150
    format(
                                                        ****',/,
    1t2, '***** A large amount of work has been expended.
    6t2, '***** (500 steps attempted)
                                                        *****')
160
    format(
    1t2, '***** The error tolerances are too stringent.
                                                        ****',/,
                                                        ****')
    6t2, '***** Error tolerances increased.
    format(t2,'***** Rwork(12) = ',g15.6,t55,'*****')
165
170
   format(
    1t2, '***** The local error test cannot be satisfied
                                                        ****',/,
                                                       ****',/,
    1t2,'***** because you specified a zero component in ae
                                                        ****',/,
    1t2, '***** and the corresponding computed solution
                                                        ****',/,
    1t2, '***** component is zero. Thus, a pure relative
                                                        *****)
    1t2, '***** test is impossible for this component.
180
   format(
    lt2,'***** DDEBDF has repeated convergence test failures *****',/,
                                                         *****')
    6t2, '***** on the last attempted step.
190
    format(
    1t2, '***** DDEBDF has repeated error test failures on the *****',/,
                                                         ****')
    6t2, '***** last attempted step.
200
   format(
    1t2, '***** The code has encountered trouble from which
                                                         ****',/,
    1t2, '***** it cannot recover. A message is printed
                                                         ****',/,
    1t2, '***** explaining the trouble and control is returned *****',/,
                                                        ****',/,
    1t2, '***** to the calling program. For example, this
                                                        ****')
    1t2, '***** occurs when invalid input is detected.
210
   format(
    1t2, '***** Error unknown idid returned from DDEBDF
                                                        *****')
220
    format(
    1t2,'***** Halting execution.....
                                                        *****')
```

end

factln.f

```
double precision function factln(x)
C-----C
c this is a program to calculate the ln of the factorial,
c were x needs to be an integer
                      -----C
C-----
implicit double precision (a-h,o-z)
   sum0 = 0.D0
   n = int(x)
   do 100 i = 2, n
    arg = dble(i)
100
     sum0 = sum0+dlog(arg)
   factln = sum0
   return
   end
```

flash.f

```
subroutine flash (zz,temp,press,mt,xwt,ywt,ymol,avemwg,vof)
С-----С
c Flash distillation of metaplast to form liquid and tar vapor
C This subroutine calculates V/F using the Rachford-Rice equation.
C-----C
implicit double precision (a-h,o-z)
    parameter (neq1 = 16, neq2 = 12)
    double precision k(neq2),zz(neq2),z(neq2),pv(neq2)
    double precision xmol(neq2),ymol(neq2),xwt(neq2),ywt(neq2)
    double precision a1(4),a2(4),a3(4),a4(4),a5(4)
    double precision mt(neq2)
    external rach
common /cfunc/ z,k,nntot2
    common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
    common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
C. . .FGP VP correlation parameters:
    data a,b,g/87058.D0,299.D0,0.5903D0/
C. . .DIPPER TDI
             TDA
                 CPN
                       CO2
    data a1/194.22,75.248,56.405,140.54/
    data a2/-14314.,-11094.,-6444.5,-4735./
    data a3/-26.701,-6.9328,-4.8222,-21.268/
    data a4/2.2518D-2,7.8095D-19,4.8774D-18,4.0909D-2/
    data a5/1.,6.,6.,1./
    data small/1.D-16/
    data zero, one, fac, rcon/0.D0, 1.D0, 1.01325D5, 82.06D0/
    data rez,aez/1.D-12,1.D-12/
C-----C
C Calculate vapor pressures and K-values. The FGP correlation is used
C for monomers, dimers, etc. The DIPPER correlations are used for the
C CPN, CO2, TDA and TDI.
C-----C
    nntot2 = ntot2
    do 50 i = 1, ntot2
50
      z(i) = zz(i)
```

```
c...Infinite matrix and inert gas
           k(ntot2) = one/small
           k(ntot2-1) = small
c...light molecules
          do 100 i = 1, ngas
                with the DIPPER correlation
С
                pv(i+nmer) = (dexp(a1(i)+a2(i)/temp+a3(i)*dlog(temp)+a3(i))*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a3(i)*dlog(temp)+a
                                        a4(i)*temp**a5(i)))/fac
         æ
100
                k(i+nmer) = max(small,pv(i+nmer)/press)
c...mers
           do 150 i = 1,nmer
                with the FGP correlation
С
                 pv(i) = a*dexp(-b*mt(i)**g/temp)
150
                k(i) = max(small,pv(i)/press)
C-----C
c use the Rachford-Rice formulation for flash distillation, vof = V/F
C-----C
C Check mixture for subcooled liquid or superheated vapor
C-----C
           fof1 = rach(one)
           fof0 = rach(zero)
           if (fofl.gt.zero .and. fof0.gt.zero) then
С
                 the mixture is a subcooled liquid
                vof = zero
           else if (fof1.lt.zero .and. fof0.lt.zero) then
С
                the mixture is a superheated vapor
                vof = one
           else
С
                 calculate the vapor liquid split
                p0 = zero
                p1 = one
                 call zeroin (rach,p0,p1,rez,aez,iflag)
                if (iflag.eq.1 .or. iflag.eq.2 .or. iflag.eq.4) then
vof = p0
                 else
                      vof = one
                 endif
          endif
C-----C
c Now calculate molecular weight distributions on a light-gas free
С
        basis, wt fractions
С-----С
          if (vof.eq.zero) then
                mixture is a subcooled liquid
С
                avemwg = zero
                sumxwt = zero
                 do 200 i = 1,ntot2
                      xmol(i) = z(i)
                      ymol(i) = zero
                      xwt(i) = xmol(i)*mt(i)
                      ywt(i) = zero
200
                      sumxwt = sumxwt+xwt(i)
                do 250 i = 1,ntot2
250
                      xwt(i) = xwt(i)/sumxwt
           else if (vof.eq.one) then
                mixture is a superheated vapor
С
                 avemwg = zero
                 sumywt = zero
                 do 300 i = 1, ntot2
                      xmol(i) = zero
                      ymol(i) = z(i)
                      xwt(i) = zero
```

```
ywt(i) = ymol(i)*mt(i)
            sumywt = sumywt+ywt(i)
300
            avemwg = avemwg+ymol(i)*mt(i)
         do 350 i = 1, ntot2
350
            ywt(i) = ywt(i)/sumywt
      else
С
         mixture is two phase
         sumxwt = zero
         sumywt = zero
         avemwg = zero
         do 400 i = 1, ntot2
            xmol(i) = z(i)/((k(i)-one)*vof+one)
            ymol(i) = k(i)*xmol(i)
            xwt(i) = xmol(i)*mt(i)
            ywt(i) = ymol(i)*mt(i)
            sumxwt = sumxwt + xwt(i)
            sumywt = sumywt + ywt(i)
400
            avemwg = avemwg+mt(i)*ymol(i)
         do 450 i = 1,ntot2
            xwt(i) = xwt(i)/sumxwt
450
            ywt(i) = ywt(i)/sumywt
      endif
      return
      end
```

flow.f

subroutine flow(y,w,mt,tp,ms,ml,mg,mi,p,twout) C-----C C This program updates the overall mass fractions, mass, pressure and C gas mass fraction to account for flow/confinement. C---------C implicit double precision (a-h,o-z) parameter (neq1 = 16, neq2 = 12) double precision ms,ml,mg,mwv,mp0,mi double precision y(neq1),twout(neq2) double precision w(neq2),mt(neq2),win(neq2),wout(neq2),ywt(neq2) common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigpl,siginv,sigpl2 common /cdbl7/ mp0,Vol,conf,fli,fac common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,cdif common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2 data zero, one, two /0.D0, 1.D0, 2.D0/ data half, small /0.5D0, 1.D-20/ c...[Rg] = cm3*atm/mol/K data Rg /82.057841D0/ save C-----C C This program updates the overall mass fractions, mass, pressure and C gas mass fraction to account for flow/confinement. C------C-----C C Calculate mass in C-----C call masin(tp,ntot2,mt,ywt,win) do 100 i = 1,ntot2 100 w(i) = w(i) + win(i)C-----C C Calculate the different phases

```
C-----
           -----C
   call phases(w,mt,tp,press,mg,ml,ms,mwv,vg,comp,ywt)
   press = mg*rg*tp/mwv/vg*comp
С-----С
C Calculate mass out
С-----С
   call masout(mg,tp,mwv,comp,ywt,vg,ntot2,wout)
   do 150 i = 1,ntot2
150
     twout(i) = twout(i)+max(wout(i),zero)
C-----C
C Update pressure and calculate the inert that would be there
С-----С
   press = mg*rg*tp/mwv/vg*comp
   mi = pamb*vg*mt(ntot2)/rg/tp/comp
C-----
                        -----C
C Calculate new overall mass gases and mers
C-----C
   do 200 i = 1,ntot2
200
   w(i) = max(w(i)-wout(i), zero)
С-----С
C Calculate moles of bridges, side chains, and sites
C-----C
   call mwavg(y,fsit,fbrg,fsch,flm)
   call masbsr(w,mt,fsit,fbrg,fsch,p,brem,drem,srem)
   call masbsr(win,mt,fsit,fbrg,fsch,p,bin,din,sin)
   call masbsr(wout, mt, fsit, fbrg, fsch, p, bout, dout, sout)
   borig = max(brem-bin+bout,small)
   dorig = max(drem-din+dout,small)
   sorig = max(srem-sin+sout,small)
C-----
                        -----C
C Calculate populations of bridges, side chains, and sites
   -----^
C----
   do 300 i = 1, nbrg
    y(i) = max(y(i)*(one-bout/borig+bin/borig),zero)
300
   do 400 i = nbrg+1,nbrg+nsch
400
    y(i) = max(y(i)*(one-dout/dorig+din/dorig),zero)
   do 500 i = nbrg+nsch+1,ncom
500
    y(i) = max(y(i)*(one-sout/sorig+sin/sorig),zero)
C-----C
C Update light molecule populations
C-----C
   do 600 i = 1,ngas
600
    y(ncom+i) = w(i+nmer)/mt(i+nmer)/fac
   return
   end
```

func.f

```
subroutine func (time,y,ydot,rpar,ipar)
С-----С
C This subroutine calculates time derivatives
C-----C
C ydot(i) = derivative of y(i) in time
C-
 -----C
y(1) = L1; y(2) = L2; y(3) = L3; y(4) = L4
С
С
 v(5)
   = D1
      i y(6) = D2 i y(7) = D3
                   ; y(8)
                      = D4
 y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
С
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
C-----C
```

```
implicit double precision (a-h,o-z)
    parameter (negl = 16, maxt = 4000)
    double precision y(neq1),ydot(neq1)
    double precision ygen(neq1)
common /cttime/ tim(maxt),tem(maxt),timax,ntim
. . . . . . . .
    data zero/0.0D0/
c...Remove any negative values (from numerical round off)
    do 50 i = 1, neq1
50
      y(i) = dmax1(y(i), zero)
C...calculate particle temperature
    t = tfun(time,ntim,tim,tem)
    call masgen(t,y,ygen)
c...set up mass balance equations
    do 100 i = 1, negl
100
      ydot(i) = yqen(i)
    return
    end
```

gamln.f

double precision function gamln3(x) C-----C С this is a program to calculate the ln of the gamma function, taken from Abramowitz, p. 257, 6.1.41 С this correlation is valid when x is above 3.0 С for x between 2.0 and 3.0 delete the bottom two lines in the function С for x between 1.0 and 2.0 delete the bottom three lines in the function С C-----C implicit double precision (a-h,o-z) С none C. . . DATA STATEMENTS. . data pi/3.14159265358979D0/ gamln3 = (x-.5)*dlog(x)-x+.5*dlog(2.*pi)+1./(12.*x)-1./(360.*x**3)+1./(1260.*x**5)-1./(1680.*x**7) æ & +1./(1188.*x**9)-691./(360360.*x**11) +1./(156.*x**13)-3617./(122400.*x**15) & +43867./(244188.*x**17)-174611./(125400.*x**19) & return end

init.f

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```
common /cdbl2/ L10,L20,L30,L40
     common /cdbl3/ mw(neq1),mwinf,mwinert
     common /cdbl4/ a(nrxn),e(nrxn),esig
     common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
     common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
     common /cdbl7/ mp0,Vol,conf,fli,fac
     common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,hbas
     common /cint1/ iprint,ntmax
     common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
     common /cttime/ tim(maxt),tem(maxt),timax,ntim
data half, one/0.5D0, 1.0D0/
C-----C
C Open input and output files
C-----C
     open (unit = nin,file = 'mtpuf.in', status = 'old')
     open (unit = 21, file = 'outkin',status = 'unknown')
     write(21,3000)
     open (unit = 22, file = 'outmas', status = 'unknown')
     write(22,4000)
     open (unit = 26, file = 'outsol',status = 'unknown')
     write(26,5000)
C-----
                        -----C
C Begin reading data from cpuf.in
C-----C
     read (nin,*) nsay
     do 100 n = 1, nsay
100
      read (nin,1000) csay
C average coordination number
     read (nin,*) sigp1
C Number of bridge types
     read (nin,*) nbrg
C Initial urethane bridge population and molecular weight
     read (nin,*) L10,mw(1)
C Initial aminourethane bridge population and molecular weight
     read (nin, *) L20,mw(2)
C Initial diamine bridge population and molecular weight
     read (nin,*) L30,mw(3)
C Initial adipate bridge population and molecular weight
     read (nin,*) L40,mw(4)
C Number of side chain types
     read (nin,*) nsch
C Initial isocyanate side chain and molecular weight
     read (nin,*) D10,mw(5)
C Initial OH side chain and molecular weight
     read (nin,*) D20,mw(6)
C Initial amino urethane side chain and molecular weight
     read (nin,*) D30,mw(7)
C Initial diamine side chain and molecular weight
     read (nin,*) D40,mw(8)
C Initial CH2 radical side chain and molecular weight
     read (nin,*) D50,mw(9)
C Initial CH2O radical side chain and molecular weight
     read (nin,*) D60,mw(10)
C Number of site types
     read (nin,*) nsit
C Site 1 population and molecular weight (TMP)
     read (nin,*) S10,mw(11)
C Site 2 population and molecular weight (DEG)
     read (nin,*) S20,mw(12)
C Number of light molecule types
     read (nin,*) ngas
C Initial TDI fraction and molecular weight
```

```
read (nin,*) TDI0,mw(13)
C Initial TDA fraction and molecular weight
     read (nin,*) TDA0,mw(14)
C Initial CPN fraction and molecular weight
     read (nin,*) CPN0,mw(15)
C Initial CO2 fraction and molecular weight
     read (nin,*) CO20,mw(16)
C Number of mer size to be considered in the calculations
     read (nin,*) nmer
c Calculate variables for convenience
     ncom = nbrg+nsch+nsit
     nreac = ncom+ngas
     ntot = nreac+nmer+2
     ntot2 = ngas+nmer+2
C Molecular weight of infinite polymer, g/mol
     read (nin,*) mwinf
C Molecular weight and flowrate of inert atmosphere, g/sec, g/mol
     read (nin,*) fli,mwinert
C Mass and density of initial polymer (mers, infinite matrix
C and light molecules), g, g/cm3 \,
     read (nin,*) mp0,rhos
C Volume in interest and confinement, cm3, unitless
     read (nin,*) Vol,conf
C Ratio of specific heats and ambient pressure, unitless, atm
      read (nin,*) gamma,pamb
C Diameter and coefficient of orifice, cm and unitless
     read (nin,*) dorf,corf
C Basket height, cm
     read (nin,*) hbas
C Kinetic coefficients
     read (nin,*) (a(i), i = 1,4)
     read (nin, *) (a(i), i = 5, 8)
     read (nin, *) (a(i), i = 9, nrxn)
     read (nin,*) (e(i), i = 1,4)
     read (nin, *) (e(i), i = 5, 8)
     read (nin, *) (e(i), i = 9, nrxn)
     read (nin,*) esig
C Pressure in atmospheres
     read (nin,*) press
C Read in critical pressures, critical temperatures and accentric factors
      do 200 i = 1,ngas
200
        read (nin,*) tc(i+nmer),pc(i+nmer),omega(i+nmer)
c Mer sizes
     read (nin,*) tc(1),pc(1),omega(1)
     read (nin, *) tc(2),pc(2),omega(2)
     read (nin, *) tc(3),pc(3),omega(3)
C As a first approx., set all n-mers above a 3-mer to the 3-mer values
      do 250 i = 4,nmer
         tc(i) = tc(3)
         pc(i) = pc(3)
250
        omega(i) = omega(3)
c Infinite Matrix
     read (nin,*) tc(ntot2-1),pc(ntot2-1),omega(ntot2-1)
c Inert gas
     read (nin,*) tc(ntot2),pc(ntot2),omega(ntot2)
C Time step for calculation
     read (nin,*) dt0,iprint,dtmax
     read (nin,*) timax
C Input temperature history
     read (nin,*) ntim
      do 300 i = 1,ntim
300
        read (nin,*) tim(i),tem(i)
C Initialize variables
```

```
rhol = rhos
     sig = sigpl-one
     siginv = one/sig
     sigp12 = sigp1/2.D0
     ntmax = idint(timax/dt0)
     dt = dmin1(dt0,dtmax)
     return
1000 format(1a80)
2000 format(15)
3000 format(' time (m)
                                L2
                       L1
                                       LЗ
                                               L4
                                                       D1
                                                               D2
    & D3
               D4
                        D5
                                D6
                                        S1
                                               S2
                                                       TDI
                                                              TDA
               CO2
                     Psys')
      CPN
    δc
4000 format(' time (m) 1mer
                                     2mer
                                               3mer
                                                          4mer
    & 5mer
               6mer
                         TDI
                                     TDA
                                               CPN
                                                         CO2
    & Inf
               He')
5000 format(' time (m) temp (C)
                                  press fmas
                                                 ms
                                                          ml
    & mg
             mi
                     mtot')
     end
```

lekes.f

```
subroutine lekes(ntot2,temp,volm,ctemp,cpress,omega,ymol,comp)
С-----С
C This subroutine converts population variables to wt fractions
C-----C
implicit double precision (a-h,o-z)
    parameter (neq2=12)
    double precision ctemp(neq2),cpress(neq2),omega(neq2),ymol(neq2)
    double precision ccomp(neq2),cvol(neq2)
    double precision cvolij(neq2,neq2),ctempij(neq2,neq2)
data zero, one, two, three, five, eight/0.D0, 1.D0, 2.D0, 3.D0, 5.D0, 8.D0/
    data half, small/0.5D0, 1.D-12/
    data Rg,eta,omegar/82.06D0,0.25D0,0.3978D0/
    data b1,b2,b3,b4/1.181193D-1,2.65728D-1,1.5479D-1,3.0323D-2/
    data bb1,bb2,bb3,bb4/2.026579D-1,3.31511D-1,2.7655D-2,2.03488D-1/
    data c1,c2,c3,c4/2.36744D-2,1.86984D-2,0.D0,4.2724D-2/
    data cc1,cc2,cc3,cc4/3.13385D-2,5.03618D-2,1.6901D-2,4.1577D-2/
    data d1,d2,be,ga/1.55488D-5,6.23689D-5,6.5392D-1,6.0167D-2/
    data dd1,dd2,bbe,gga/4.8736D-5,7.40336D-6,1.226D0,3.754D-2/
С-----С
C Calculate Critical Compressibilities and Volumes
C-----C
    do 100 i = 1, ntot2
     \operatorname{ccomp}(i) = \operatorname{dmax1}(0.2905D0 - .085D0 * \operatorname{omega}(i), \operatorname{zero})
100
     cvol(i) = ccomp(i)*Rg*ctemp(i)/cpress(i)
C-----C
C Calculate Critical Volume and Temperature cross products (ij)
С-----С
    do 200 i = 1,ntot2
      do 300 j = 1, ntot2
        cvolij(i,j) = one/eight*(cvol(i)**(one/three)+
                 cvol(j)**(one/three))**three
300
        ctempij(i,j) = (ctemp(i)*ctemp(j))**half
200 continue
C-----C
C Calculate Critical Volume, Temperature, Pressure and Omega of mixture
C-----
```

```
omegam = zero
    cvolm = zero
    do 400 i =1,ntot2
      omegam = omegam+ymol(i)*omega(i)
      do 500 j = 1, ntot2
500
        cvolm = cvolm+ymol(i)*ymol(j)*cvolij(i,j)
400
    continue
    ctempm = zero
    do 600 i = 1,ntot2
      do 700 j = 1,ntot2
700
        ctempm = ctempm+ymol(i)*ymol(j)*ctempij(i,j)*
   δ2
              cvolij(i,j)**eta
600
   continue
    ctempm = ctempm*cvolm**(-eta)
    ccompm = 0.2905D0-.085D0*omegam
    cpressm = Rg*ctempm*ccompm/cvolm
C-----C
C Calculate Reduced Volume and Temperature of mixture
С-----С
    rvol = volm*cpressm/Rg/ctempm
    rtemp = temp/ctempm
C-----
                   -----C
C Calculate Coefficients
C-----C
    B = b1-b2/rtemp-b3/rtemp**two-b4/rtemp**three
    C = c1 - c2/rtemp + c3/rtemp * * three
    D = d1 + d2 / rtemp
    BB = bb1-bb2/rtemp-bb3/rtemp**two-bb4/rtemp**three
    CC = cc1-cc2/rtemp+cc3/rtemp**three
    DD = dd1 + dd2 / rtemp
C-----C
C Calculate Compressibility of simple (0) and reference (r) fluids
С-----С
    comp0 = one+BB/rvol+CC/rvol**two+DD/rvol**five+cc4/rtemp**three
   & /rvol**two*(bbe+gga/rvol**two)*dexp(-gga/rvol**two)
   compr = one+B/rvol+C/rvol**two+D/rvol**five+c4/rtemp**three
   æ
         /rvol**two*(be+ga/rvol**two)*dexp(-ga/rvol**two)
   comp1 = (compr-comp0)/omegar
C-----C
C Calculate Compressibility
C-----C
    comp = comp0+omegam*comp1
    return
    end
```

masbsr.f

```
data zero, one, two/0.D0, 1.D0, 2.D0/
   data half,small/0.5D0,1.D-16/
С-----С
C Calculate moles of bridges, side chains and reactive caps in mers
C-----C
   bb = zero
   dd = zero
   ss = zero
   do 100 i = 1,nmer
     arg = dble(i)
      sn = arg-one
      tn = arg*(sig-one)+two
     bb = bb+mas(i)*sn/mt(i)
      dd = dd + mas(i) * tn/mt(i)
100
     ss = ss+mas(i)*arg/mt(i)
C-----C
C Calculate moles of bridges, side chains and reactive caps in infinite matrix
C-----C
   pinf = pinfin(p)
   mwexsit = fsit+sigp12*(pinf*fbrg+two*(one-pinf)*fsch)
   sitesinf = mas(ntot2-1)/mwexsit
   bridinf = sitesinf*siqp12*pinf
   sideinf = sitesinf*sigp12*(one-pinf)
   bb = bb+bridinf
   dd = dd+sideinf
   ss = ss+sitesinf
   return
   end
```

masgen.f

```
subroutine masgen(tp,y,mgen)
C-----C
C This subroutine calculates the mass generation rate term
C and updates the mass fractions of the mer sizes.
С-----С
С-----С
C y(1) = L1 ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
C-----C
implicit double precision (a-h,o-z)
   parameter (neq1 = 16, nrxn = 11, maxt = 4000)
   double precision k(nrxn),y(neq1),mgen(neq1)
   double precision L1,L2,L3,L4
common /cdbl4/ a(nrxn),e(nrxn),esig
   common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
   common /cttime/ tim(maxt),tem(maxt),timax,ntim
c...[rg]=cal/mol/K
   data zero,rg,small/0.D0,1.987D0,1.D-12/
C...calculate rate constants
   rt = rg*tp
   do 1000 i = 1,nrxn
1000 k(i) = a(i)*dexp(-(e(i))/rt)
C-----C
С
             (1\2) (3\4)
```

```
C 16 "species"
                  L1 <--> D1 + D2 <--> TDI + 2 D2
                    \setminus (5) (6\setminus7)
C 11 reactions
                     \--> L2 <--> D2 + D3
С
                     -CO2 \ (8) (9)
С
                                             (10)
                            \--> L3 --> D4 + D5 --> TDA + 2 D5
С
С
                             -CO2
С
С
                   (11)
С
                 L4 --> D5 + CPN + CO2 + D6
С-----С
C y(1) = L1 ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
  y(5) = D1; y(6) = D2; y(7) = D3; y(8)
С
                                             = D4
C y(9) = D5 ; y(10) = D6 ; y(11) = S1 ; y(12) = S2
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
  -----C
C---
c...Define variables for ease of defining rates
     L1 = y(1)
     L2 = y(2)
     L3 = y(3)
     L4 = y(4)
     D1 = y(5)
     D2 = y(6)
     D3 = y(7)
     D4 = y(8)
     TDI = y(13)
C...set up rate equations
c...bridges
     mgen(1) = -k(1)*L1+k(2)*D1*D2-k(5)*L1
     mgen(2) = +k(5)*L1-k(6)*L2+k(7)*D2*D3-k(8)*L2
     mgen(3) = +k(8)*L2-k(9)*L3
     mgen(4) = -k(11)*L4
c...side chains
     mgen(5) = +k(1)*L1-k(2)*D1*D2-k(3)*D1+k(4)*TDI*D2
     mgen(6) = +k(1)*L1-k(2)*D1*D2+k(3)*D1-k(4)*TDI*D2+k(6)*L2
            -k(7)*D2*D3
    æ
     mgen(7) = +k(6)*L2-k(7)*D2*D3
     mgen(8) = +k(9)*L3-k(10)*D4
     mgen(9) = +k(9)*L3+k(10)*D4+k(11)*L4
     mgen(10) = +k(11)*L4
c...sites
     do 1100 i = nbrg+nsch+1,ncom
1100
      mgen(i) = zero
c...light molecules
     mgen(13) = (+k(3)*D1-k(4)*TDI*D2)
     mgen(14) = (+k(10)*D4)
     mgen(15) = (+k(11)*L4)
     mgen(16) = (+k(5)*L1+k(8)*L2+k(11)*L4)
     return
     end
```

masin.f

```
double precision mp0
common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
    common /cdbl7/ mp0,Vol,conf,fli,fac
. . . . . . . . . . . . .
    data zero,one,half/0.D0,1.D0,0.5D0/
c...[Rg] = cm3*atm/mol/K
   data Rg /82.057841D0/
С-----С
C Calculate mass in due to flow
С-----С
    if (conf.eq.zero) then
      unconfined
C
      do 100 i = 1,ntot2-1
100
        msin(i) = zero
      msin(ntot2) = fli*dt*press/Rg/tp*mt(ntot2)
    else if (conf.eq.one) then
С
      confined
      do 200 i = 1, ntot2
200
        msin(i) = zero
    else
С
      partially confined
      do 300 i = 1, ntot2
300
        msin(i) = zero
    end if
    return
    end
```

masout.f

```
subroutine masout(mg,tp,mwv,comp,ywt,vg,ntot2,msout)
C23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123
C-----C
C This subroutine converts population variables to wt fractions
C-----C
C. . .VARIABLE DECLARATIONS. . . . . . . .
                                                   . . . . . . . . . . . . . . .
       implicit double precision (a-h,o-z)
       parameter (neq2 = 12)
       double precision msout(neq2),ywt(neq2)
       double precision mp0, mwv, mq, mq0, moq, moqmax
. . . .
       common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
       common /cdbl7/ mp0,Vol,conf,fli,fac
       common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf
data zero, one, half/0.D0, 1.D0, 0.5D0/
       data two,pi/2.D0,3.1415926D0/
c...[rg] = cm3*atm/mol/K [rg2] = atm2*sec2*cm4/gm/mol/K
      data rg,rg2 /82.057841D0,8.09847925D-5/
C-----C
C Calculate mass out due to flow
C-----C
      if (conf.eq.zero) then
С
          unconfined
          mq0 = mq
          mg = press/rg/tp*mwv*vg/comp
          mog = mg0-mg
       else if (conf.eq.one) then
С
          confined
          mog = zero
       else
```

```
С
        partially confined
        aorf = pi*(dorf/two)**two
        pstr = press*(two/(gamma+one))**(gamma/(gamma-one))
        prat = min(max(pamb,pstr)/press,one)
         fmog = aorf*press*dsqrt(two*gamma/(gamma-one)/(rg2/mwv*
               tp)*(prat**(two/gamma)-prat**((gamma+one)/gamma)))
    æ
        mogmax = max(mg-pamb/rg/tp*mwv*vg/comp,zero)
        mog = min(max(corf*fmog*dt,zero),mogmax)
         mg = mg - mog
      end if
     do 100 i = 1,ntot2
100
        msout(i) = mog*ywt(i)
     return
     end
```

mwavg.f

```
subroutine mwavg(y,fsit,fbrg,fsch,flm)
C-----C
C Calculates average molecular weight of bridges, side chains,
C light molecules, and reactive caps
C-----C
implicit double precision (a-h,o-z)
   parameter (neg1 = 16)
   double precision mw,lm
   double precision y(neq1)
common /cdbl3/ mw(neq1),mwinf,mwinert
    common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data zero, small/0.D0,1.D-12/
p = zero
    sum1 = zero
    do 100 i = 1,nbrg
     p = p+y(i)
100
      suml = suml+y(i)*mw(i)
    sch = zero
    sum2 = zero
    do 200 i = nbrg+1,nbrg+nsch
      sch = sch+y(i)
200
      sum2 = sum2 + y(i) * mw(i)
    sit = zero
    sum3 = zero
    do 300 i = nbrg+nsch+1,ncom
     sit = sit+y(i)
     sum3 = sum3 + y(i) * mw(i)
300
    lm = zero
    sum4 = zero
    do 400 i = ncom+1,nreac
      lm = lm+y(i)
400
      sum4 = sum4 + y(i) * mw(i)
    if (p.le.small)then
С
      there are no bridges
      fbrg = zero
      do 500 i = 1,nbrg
        fbrg = fbrg+mw(i)
500
      fbrg = fbrg/dble(nbrg)
    else
      fbrg = sum1/p
```

```
endif
      if (sch.le.small) then
С
         there are no side chains
         fsch = zero
         do 600 i = nbrg+1,nbrg+nsch
600
            fsch = fsch+mw(i)
         fsch = fsch/dble(nsch)
      else
        fsch = sum2/sch
      endif
      if (sit.le.small)then
С
         there are no sits
         fsit = zero
         do 700 i = nbrg+nsch+1,ncom
700
            fsit = fsit+mw(i)
         fsit = fsit/dble(nsit)
      else
         fsit = sum3/sit
      endif
      if (lm.le.small)then
         there are no light molecules
С
         flm = zero
         do 800 i = ncom+1,nreac
800
            flm = flm+mw(i)
         flm = flm/dble(ngas)
      else
        flm = sum4/lm
      endif
      return
      end
```

perk.f

```
subroutine perk(y,psys,ft,mt,ftinf,totmas)
С-----С
C Calculates weight fraction and molecular weight of each tar bin
C using population parameters
С-----С
implicit double precision (a-h,o-z)
    parameter (neq1 = 16, neq2 = 12)
    double precision ft(neq2),mt(neq2),y(neq1)
common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
    common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
C. . .DATA STATEMENTS. . . . . . . . . . . . .
                              . . . . . . . . . . . . .
    data zero, one, two/0.D0, 1.D0, 2.D0/
    data half,small/0.5D0,1.D-12/
C. . . EXECUTABLE STATEMENTS. . . . .
                              . . . . . . . . . . . . . . .
    call mwavg(y,fsit,fbrg,fsch,flm)
    totmas = fsit+sigp12*(fbrg*psys+two*(one-psys)*fsch)
C-----C
C Calculate perk parameters
C-----C
    mt(1) = fsit+sigp1*fsch
    ft(1) = (one-psys)**sigp1*mt(1)/totmas
    tn = two*(sig-one)+two
    mt(2) = two*fsit+fbrg+tn*fsch
    ft(2) = sigp12*psys*(one-psys)**tn*mt(2)/totmas
    ftsum = ft(1)+ft(2)
    do 100 n = 3, nmer
```

```
arg = dble(n)
        sn = arg-one
         tn = arg*(sig-one)+two
C. . . gamln3 is the ln of the gamma function very accurate for x>3
        fgam = dexp(gamln3(arg*sig+two)-gamln3(arg)-gamln3(tn+one))
        bnn = fgam*sigp1/(arg*sig+one)
         qn = bnn*(psys**sn)*((one-psys)**tn)/arg
c mt(n) = molecular weight of each polymer fragment bin
        mt(n) = arg*fsit+sn*fbrg+tn*fsch
c ft(n) = weight fraction of each polymer fragment bin
        ft(n) = qn*mt(n)/totmas
         ftsum = ftsum+ft(n)
100
      ftinf = max(one-ftsum,zero)
     return
      end
```

phases.f

```
subroutine phases(w,mt,tp,press,mg,ml,ms,mwv,vq,comp,ywt)
C23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x12
C-----C
C This subroutine calculates the distribution between the gas, "liquid"
C and "solid" phases, as well as the compressibility, volume and
C molecular weight of the gas phase
C-----
                                        -----C
implicit double precision (a-h,o-z)
      parameter (neq1 = 16, neq2 = 12)
      double precision w(neq2),mt(neq2)
      double precision z(neq2),xwt(neq2),ywt(neq2),ymol(neq2)
      double precision mp0,mtot,mwf,mwv,ms,ml,mg
common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
      common /cdbl7/ mp0,Vol,conf,fli,fac
      common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf
      common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data zero, one, half, small/0.D0, 1.D0, 0.5D0, 1.D-20/
      data two,pi,ucon/2.D0,3.1415926D0,1.0066032D7/
c...[Rg] = cm3*atm/mol/K
     data Rg /82.057841D0/
C-----C
C Convert to mole fractions for flash calculation
C-----C
     mtot = zero
     ftot = zero
      do 100 i = 1,ntot2-2
        z(i) = w(i)/mt(i)
        mtot = w(i) + mtot
100
         ftot = ftot + z(i)
      z(ntot2-1) = zero
     z(ntot2) = w(ntot2)/mt(ntot2)
      ftot = ftot+z(ntot2)
     mtot = mtot + w(ntot2)
      mwf = zero
      do 200 i = 1,ntot2
         z(i) = z(i)/ftot
200
        mwf = mwf+mt(i)*z(i)
C-----C
C Flash calculation
C-----C
      call flash (z,tp,press,mt,xwt,ywt,ymol,mwv,vof)
```

```
C-----C
C Calculate mass of gas, "liquid" and "solid"
С------С
   mg = mtot*vof*mwv/mwf
   ms = w(ntot2-1)
  ml = max(mtot-mg,zero)
C-----C
C Calculate molar volume and compressibility of gas
C-----C
   vs = ms/rhos
   vl = ml/rhol
   vg = Vol-vs-vl
   rhog = mg/vg
   volm = mwv/rhog
   call lekes(ntot2,tp,volm,tc,pc,omega,ymol,comp)
   return
   end
```

pinfin.f

```
double precision function pinfin(psys)
C-----C
  This program calculates the p of the infinite matrix from
С
 the p of the system
C
С-----С
implicit double precision (a-h,o-z)
common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
    common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data zero, one, two /0.D0,1.D0,2.D0/
    psys = max(min(psys,one),zero)
    if (psys.le.pcrit) then
      pinfin = dble(nmer)/(dble(nmer+one))/sigp12
      return
    end if
    sig = sigp1-one
    tn = two*(sig-one)+two
    fsum = (one-psys)**siqp1+siqp1*psys*(one-psys)**tn
    sum0 = sigp1*psys*(one-psys)**tn/two
    do 100 n = 3, nmer
      arg = dble(n)
      sn = arg-one
      tn = arg*(sig-one)+two
C. . . . gamln is the ln of the gamma function
      fgam = dexp(gamln3(arg*sig+two)-gamln3(arg)-gamln3(tn+one))
      bnn = fgam*sigp1/(arg*sig+one)
      fsum = fsum+bnn*(psys**sn)*((one-psys)**tn)
100
      sum0 = sum0+bnn*(psys**sn)*((one-psys)**tn)*(arg-one)/arg
    finf = one-fsum
    pinfin = (psys-two/sigp1*sum0)/finf
    return
    end
```

popbal.f

```
C-----C
C This subroutine calculates the population balance theory results
С------С
implicit double precision (a-h,o-z)
    parameter (neq1 = 16, neq2 = 12)
    double precision w(neq2),wgen(neq2),y(neq1),ygen(neq1),yold(neq1)
    double precision tau(neq2),ft(neq2),mt(neq2),mtn(neq2)
    double precision mw, mwexsit, mwexsitn, mp, mtot, mtot0
   с. .
    common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
    common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data zero, one, two, four/0.D0, 1.D0, 2.D0, 4.D0/
    data half,small/0.5D0,1.D-20/
   data Rg/8.314D0/
C-----C
C Calculate the relative changes in psys, ssys and rsys.
C-----C
   pold = max(pold,small)
   psys = max(psys,small)
   pp = (psys-pold)/pold
C-----C
C Start population balance theory
С-----С
    call perk(yold,pold,ft,mt,ftinf,totmas)
c...Calculate the properties of the infinite matrix % \left( {{{\boldsymbol{x}}_{i}}} \right)
   pinf = pinfin(pold)
    call mwavg(yold,fsit,fbrg,fsch,flm)
   mwexsit = fsit+sigp12*(pinf*fbrg+two*(one-pinf)*fsch)
    if (pp .le. zero) then
c...Bridges breaking or nothing
     dp = -pp
С-----С
C Bethe lattice statistics of before reactions
С-----С
      if (psys .lt. pcrit) then
        check = one
        goto 300
      end if
c...Subtract phantom mers from existing mers
      mp = w(ntot2-1)/ftinf
      do 200 i = 1,nmer
200
       w(i) = w(i) - ft(i) * mp
c...Correct mass of nmers for reaction
      do 400 i = 1, nmer-1
300
        sum1 = zero
        arg2 = dble(i)
        sum1 = sum1+w(i)*(one-dp)**(arg2-one)
        do 500 j = i+1,nmer
          sum2 = zero
          arg1 = dble(j)
        do 600 k = 1, j-i
            arg3 = dble(k)
            cnmbr = (arg3+one)*dexp(factln(arg1-arg2-one)-
                  factln(arg3-one)-factln(arg1-arg2-arg3))
   &
600
            sum2 = sum2+cnmbr*(dp)**arg3*(one-dp)**(arg1-arg3-one)
500
          suml = suml+w(j)*mt(i)/mt(j)*sum2
400
        w(i) = sum1
      w(nmer) = w(nmer)*(one-dp)**(nmer-1)
C-----C
C Bethe lattice statistics of after reactions
С-----С
```

```
call perk(yold,psys,ft,mt,ftinf,totmasn)
c...Check if below p critical
         if (check .eq. one) goto 3000
         if (psys .lt. pcrit) then
            do 800 i = 1,nmer
800
               ft(i) = ft(i)/(one-ftinf)
          ftinf = zero
         end if
c...Add phantom mers back
         do 900 i = 1,nmer
900
            w(i) = w(i)+ft(i)*mp*totmasn/totmas
      else
         dsc = max(min((psys-pold)/(one-pold),one),zero)
c...Extreme cases
         if (dsc .eq. one) then
            do 1000 n = 1, nmer
1000
               wgen(n) = -one*w(n)
            goto 2000
         else if (dsc .eq. zero) then
            goto 3000
         end if
c...Shorten the step taken to ensure higher accuracy
         nsteps = min(1,dlog(pp)/dlog(1.0015))
С
         do iii = 1,nsteps
С
c...Calculate the bridges and side chains
         do 1100 n = 1, nmer
            arg = dble(n)
1100
               tau(n) = (arg*(sig-one)+two)
         sitesinf = w(ntot2-1)/mwexsit
         sideinf = sitesinf*sigp1*(one-pinf)
c...Calculate the total number of reacted side chains to bridges
         trs = zero
         do 1200 n = 1, nmer
1200
            trs = trs+tau(n)*w(n)/mt(n)*dsc
         trs = max(trs+dsc*sideinf,small)
c...Calculate the mass generated for each mer size
         nmax = nmer
         rnmax = dble(nmer)
c...first order terms
         do 1300 n = 1,nmax
            wgen(n) = w(n)*((one-dsc)**tau(n)-one)
1300
c...second order terms
         nmax2l = int(rnmax/two)
         do 1500 i = 1, nmax21
            n = 2*i
            wgen(n) = wgen(n)+mt(n)*tau(i)*tau(i)*(one-dsc)**(tau(i))
     &
                      +tau(i)-two)*dsc**two*w(i)/mt(i)
     &
                      *w(i)/mt(i)/trs/two
           do 1600 j = i+1, nmax-i
               n = i + j
               wgen(n) = wgen(n)+mt(n)*tau(i)*tau(j)*(one-dsc)**(tau(i)
                          +tau(j)-two)*dsc**two*w(i)/mt(i)
     &
                          *w(j)/mt(j)/trs
     &
1600
            continue
1500
         continue
c... third order terms
         do 1700 i = 1,nmax-2
            arg = dble(nmax-i)
            nmaxi2l = int(arg/two)
            do 1800 j = 1, nmaxi21
               n = i + 2*j
               wgen(n) = wgen(n)+mt(n)*tau(i)*(tau(i)-one)*tau(j)
                         *tau(j)*(one-dsc)**(tau(i)+tau(j)+tau(j)
     &
```

```
261
```

```
-four)*dsc**four*w(i)/mt(i)*w(j)
     &
     &
                          /mt(j)*w(j)/mt(j)/trs**two/two
            do 1900 k = j+1, nmax-i-j
               n = i + j + k
               wgen(n) = wgen(n)+mt(n)*tau(i)*(tau(i)-one)*tau(j)
                          *tau(k)*(one-dsc)**(tau(i)+tau(j)+tau(k)
     &
                          -four)*dsc**four*w(i)/mt(i)*w(j)
     æ
                          /mt(j)*w(k)/mt(k)/trs**two
     &
1900
               continue
1800
            continue
1700
         continue
c...Add in the mass generated from reaction
2000
        do 2100 n = 1,nmer
2100
           w(n) = w(n) + wgen(n)
      end if
c...Update the old parameter for next time
3000 pold = psys
c...Update masses for release or reattachment of gases
      call perk(y,psys,ft,mtn,ftinf,totmas)
      do 3100 i = 1,nmer
         w(i) = w(i) * mtn(i) / mt(i)
3100
         mt(i) = mtn(i)
      return
      end
```

popmas.f

```
subroutine popmas(y,yold,psyso,w,mt)
C-----C
C This subroutine converts population variables to wt fractions
C-----C
implicit double precision (a-h,o-z)
   parameter (neq1 = 16, neq2 = 12)
   double precision y(neq1),yold(neq1)
   double precision w(neq2),mt(neq2)
   double precision mp0
common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigpl,siginv,sigpl2
   common /cdbl7/ mp0,Vol,conf,fli,fac
   common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data zero, one, two, four/0.D0, 1.D0, 2.D0, 4.D0/
   data half,small/0.5D0,1.D-20/
C-----C
C Calculate relative change in bridges, side chains, and light molecules
C-----C
   psyso = max(psyso,small)
   p = zero
   pold = zero
   do 100 i = 1,nbrg
     p = p + y(i)
100
     pold = pold+yold(i)
   if (pold .le. small) then
     pold = small
   end if
   rounderr = 1.d-10
   pp = (p-pold)/pold
   if (abs(pp).le.rounderr) pp = zero
   psys = psyso*(one+pp)
```
```
tmas = zero
   do 200 i = 1,ntot2-1
200
    tmas = tmas+w(i)
   call popbal(w,yold,psyso,y,psys,mt)
С-----С
C Calculate masses of the gases
С-----С
   do 400 i = 1, ngas
400
    w(i+nmer) = y(i+ncom)*mt(i+nmer)*fac
С-----С
C Calculate masses of the infinite matrix
C------^
   tmasp = zero
   do 500 i = 1, ntot2-2
    w(i) = max(w(i), zero)
500
     tmasp = tmasp+w(i)
   w(ntot2-1) = max(tmas-tmasp,zero)
   return
   end
```

rach.f

```
double precision function rach(vof)
C-----C
c calculate sum (Eq. 7-11 on pg. 274, Equilibrium-Stage Separation
C Operations in Chemical Engineering, by Henley and Seader, 1971)
C-----
                             -----C
                       _ _ _ _ _ _ _ _ _ _ _ _
implicit double precision (a-h,o-z)
   parameter (neq2 = 12)
   double precision k(neq2),z(neq2)
common /cfunc/ z,k,nntot2
data zero,one /0.D0,1.D0/
   rach = zero
   do 100 i =1,nntot2
     rach = rach + z(i)*(one-k(i))/(one+vof*(k(i)-one))
     if (rach.ge.1.d3) return
100
   continue
   return
   end
```

rpcrit.f

```
double precision function rpcrit(pcrit)
С-----С
c This program is set up in a form best suited for finding the zero
C-----C
implicit double precision (a-h,o-z)
common /cdbl5/ dt,dt0,dtmax,press,ppcrit,sig,sigpl,siginv,sigpl2
   common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data tol /1.d-8/
   data zero, one, two /0.D0,1.D0,2.D0/
   tt2 = two*(sig-one)+two
   fsum = (one-pcrit)**sigp1+sigp1*pcrit*(one-pcrit)**tt2
   do 100 n=3,nmer
     arg = dble(n)
```

```
sn = arg-one
tn = arg*(sig-one)+two
C. . . gamln is the ln of the gamma function
fgam = dexp(gamln3(arg*sig+two)-gamln3(arg)-gamln3(tn+one))
bnn = fgam*sigp1/(arg*sig+one)
100 fsum = fsum+bnn*(pcrit**sn)*((one-pcrit)**tn)
finf = one-fsum
rpcrit = tol-finf
return
end
```

sinit.f

```
subroutine sinit (info,atol,rtol)
C-----C
C This subroutine initializes the parameters used by the solver ddebdf
C-----C
implicit double precision (a-h,o-z)
  dimension info(15)
C The following two statements should be put in the main program (puf)
  parameter (neq = 15, lrw = 250+neq*(10+neq), liw = 56+neq)
С
  dimension rwork(lrw), iwork(liw)
C
C None
C None
С-----<sup>с</sup>
C Begin executable statements
С-----С
C Function routine will be "func"
  do 100 i=1,15
100
    info(i) = 0
  atol = 1.D-10
  rtol = 1.D-10
  return
  end
```

tfun.f

```
double precision function tfun(time,nfp,timpts,tmppts)
C------C
C Linear interpolation of temperature
С
 input
    time
        - Time for temperature BC function
С
С
    nfp
         - Number of function points
    timpts - Array containing function times
С
    tmppts - Array containing function temperatures
С
С
c output
С
    return tfun - temperature at time
C-----C
implicit double precision (a-h,o-z)
    dimension timpts(*),tmppts(*)
    do 10 i=2,nfp
      if (timpts(i).ge.time) then
        dtdt = (tmppts(i)-tmppts(i-1))/(timpts(i)-timpts(i-1))
```

```
tfun = tmppts(i-1) + dtdt*(time-timpts(i-1))
    return
    endif
10 continue
if (time.le.timpts(1)) then
    tfun = tmppts(1)
    return
end if
if (time.ge.timpts(nfp)) then
    tfun = tmppts(nfp)
    return
end if
stop
end
```

zeroer.f

```
SUBROUTINE ZEROER (IFLAG)
C-----C
C This subroutine outputs error messages for the ZEROIN subroutine.
                                              С
С-----С
C Input Description
                                               C
C -----
      ----- ^
C IFLAG Error Flag for ZEROIN
                                               С
C------C
   IMPLICIT DOUBLE PRECISION (A-H,O-Z), INTEGER (I-N)
C------C
C Write Error Messages for ZEROIN
                                               С
WRITE(6,110) IFLAG
   IF (IFLAG .EQ. 2) THEN
    WRITE(6,120)
   ELSEIF (IFLAG .EQ. 3) THEN
    WRITE(6,130)
   ELSEIF (IFLAG .EQ. 4) THEN
    WRITE(6,140)
   ELSEIF (IFLAG .EQ. 5) THEN
    WRITE(6,150)
   ELSE
    WRITE(6,160)
   ENDIF
   RETURN
C-----C
 1 2 3 4 5 6 7 C
С
C23456789X123456789X123456789X123456789X123456789X123456789X123456789X123456789X123
C-----C
С
                    FORMATS
                                               С
C------C
110 FORMAT(/,
  1T2, '***** Error Flag = ', I6, '
                                         * * * * * ! )
120
  FORMAT (
   1T2, '***** F(B) =0. However, the interval (B,C) may not *****',/,
   2T2, '***** have collapsed to the requested tolerance.
                                         ****')
130
   FORMAT (
   1T2, '***** B may be near a singular point of F(X). The
                                         *****',/,
                                         ****',/,
   2T2, '***** interval (B,C) collapsed to the requested
                                         ****',/,
   3T2, '***** tolerance and the function changes sign in
                                         ****',/,
   4T2, '***** (B,C), but F(X) increased in magnitude as
                                         ****',/,
   5T2, '***** (B,C) collapsed, i.e. ABS(F(B OUT)) >
   6T2, '***** MAX(ABS(F(B IN)), ABS(F(C IN)))
                                         ****')
140
  FORMAT (
```

	1T2,'****	No change in sign of F(X) was found Although	****',/
	2T2,'*****	the interval (B,C) collapsed to the requested	****',/
	3T2,'****	tolerance. The user must examine this case	****',/
	4T2,'****	and decide whether B is near a local minimum	****',/
	5T2,'*****	of $F(X)$, or B is near a zero of even	****',/
	бТ2,'****	multiplicity, or neither of these.	****')
150	FORMAT (
	1T2,'****	Too many (> 500) function evaluations used.	****')
160	FORMAT (
	1T2,'****	Error unknown IFLAG returned from ZEROIN	****')
	END		

zeroin.f

```
SUBROUTINE ZEROIN(F,B,C,RE,AE,IFLAG)
     IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C##
     EXTERNAL F
C##
С
С
     SANDIA MATHEMATICAL PROGRAM LIBRARY
С
     APPLIED MATHEMATICS DIVISION 2646
С
     SANDIA LABORATORIES
С
     ALBUQUERQUE, NEW MEXICO 87185
     CONTROL DATA 6600/7600 VERSION 8.1 AUGUST 1980
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                    A PRIME CONTRACTOR
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                        * UNITED STATES
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                            DEPARTMENT
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С
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С
      * BY THE UNITED STATES GOVERNMENT. NEITHER THE UNITED *
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С
         STATES NOR THE UNITED STATES DEPARTMENT OF ENERGY,
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      * EMPLOYEES, MAKES ANY WARRANTY, EXPRESS OR IMPLIED, OR
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C	BASED ON A METROD BI I U DERRER
С	WRITTEN BY L F SHAMPINE AND H A WATTS
С	MODIFIED FOR THE MATH LIBRARY BY C B BAILEY
С	
C C	
C	ZEROIN SEARCHES FOR A ZERO OF A FUNCTION F(X) BETWEEN
С	THE GIVEN VALUES B AND C UNTIL THE WIDTH OF THE INTERVAL
С	(B,C) HAS COLLAPSED TO WITHIN A TOLERANCE SPECIFIED BY
C	THE STOPPING CRITERION $ABS(B-C)$ I.E. 2 *(RW*ABS(B)+AE)
a	THE DEFINITION OF THE CONTRACTOR OF THE CONTRACT
C	THE METHOD USED IS AN EFFICIENT COMBINATION OF BISECTION AND
C	THE SECANT RULE. IN ORDER TO INSURE THAT ZEROIN WILL CONVERGE
С	TO A ZERO, THE USER SHOULD PICK VALUES FOR B AND C AT WHICH
С	THE FUNCTION DIFFERS IN SIGN.
C	
с а	
C ~	DESCRIPTION OF ARGUMENTS
C	F, B, C, RE AND AE ARE INPUT PARAMETERS
С	B,C AND IFLAG ARE OUTPUT PARAMETERS
С	F - NAME OF THE REAL VALUED EXTERNAL FUNCTION. THIS NAME
С	MUST BE IN AN EXTERNAL STATEMENT IN THE CALLING
č	DOCODAM E MILICIPE A FINISHIAN IN THE CALLING
	FROGRAM. F MUSI DE A FUNCTION OF UNE REAL ARGUMENT.
C	B - ONE END OF THE INTERVAL (B,C). THE VALUE RETURNED FOR
С	B USUALLY IS THE BETTER APPROXIMATION TO A ZERO OF F.
С	C - THE OTHER END OF THE INTERVAL (B,C)
C	RE - RELATIVE ERROR USED FOR RW IN THE STOPPING CRITERION
C	TE THE DEGLEGATED DE IS LESS THAN MACHINE DESISION
	IF THE RECEIPTED RE IS LESS THAN MACHINE PRECISION,
C	THEN RW IS SET TO APPROXIMATELY MACHINE PRECISION.
С	AE - ABSOLUTE ERROR USED IN THE STOPPING CRITERION. IF THE
С	GIVEN INTERVAL (B,C) CONTAINS THE ORIGIN, THEN A
С	NONZERO VALUE SHOULD BE CHOSEN FOR AE.
C	IFLAC - A STATUS CODE USER MIST CHECK IFLAC AFTER FACH CALL
	IFLAG - A STATUS CODE. OBER MOST CHECK TFLAG AFTER EACH CALL.
C	CONTROL RETURNS TO THE USER FROM ZEROIN IN ALL CASES.
С	XERROR DOES NOT PROCESS DIAGNOSTICS IN THESE CASES.
С	1 B IS WITHIN THE REQUESTED TOLERANCE OF A ZERO.
С	THE INTERVAL (B.C.) COLLAPSED TO THE REQUESTED
Ċ	TOLERANCE THE FUNCTION CHANGES SIGN IN (B.C.) AND
	EXAMPLE THE FUNCTION CHARGED STOLEN IN (D,C), AND
C	F(X) DECREASED IN MAGNITUDE AS (B,C) COLLAPSED.
С	2 F(B) = 0. However, the interval (B,C) may not have
С	COLLAPSED TO THE REQUESTED TOLERANCE.
С	3 B MAY BE NEAR A SINGULAR POINT OF $F(X)$.
C	THE INTERVAL (B.C.) COLLADSED TO THE RECUESTED
	THE ENTERVED (D,C) COLLERING TO THE REQUESTED
Ċ	TOLERANCE AND THE FUNCTION CHANGES SIGN IN (B,C) BUT
С	F(X) INCREASED IN MAGNITUDE AS (B,C) COLLAPSED,I.E.
С	ABS(F(B OUT)) .GT. $MAX(ABS(F(B IN)),ABS(F(C IN)))$
С	4 NO CHANGE IN SIGN OF $F(X)$ WAS FOUND ALTHOUGH THE
C	INTERVAL, (B.C.) COLLADSED TO THE REGULESTED TO FRANCE
<u> </u>	THISKING (5,C) COLLER DED TO THE REQUESTED TODERANCE.
	ITE USER MUSI EXAMINE IHIS CASE AND DECIDE WHETHER
C	B IS NEAR A LOCAL MINIMUM OF F(X), OR B IS NEAR A
С	ZERO OF EVEN MULTIPLICITY, OR NEITHER OF THESE.
С	5 TOO MANY (.GT. 500) FUNCTION EVALUATIONS USED.
С	
c	DEFEDENCES
C	I. L F SHAMPINE AND H A WATTS, ZEROIN, A ROOT-SOLVING CODE,
С	SC-TM-70-631, SEPT 1970.
С	2. T J DEKKER, FINDING A ZERO BY MEANS OF SUCCESSIVE LINEAR
С	INTERPOLATION. *CONSTRUCTIVE ASPECTS OF THE FUNDAMENTAL
C	TUPODEM OF ALGEDDAY EDITED BY DIFTON AND DIFFUTATION
	INEUREM OF ALGEDRA", EDITED BI B DEJUN AND P HENRICI, 1969.
Ċ	
С	
С	ER IS TWO TIMES THE COMPUTER UNIT ROUNDOFF VALUE WHICH IS
С	DEFINED HERE BY THE FUNCTION BEMACH (REPLACES D1MACH)
Ċ	
<u> </u>	

```
ER = 2.0D0 * BBMACH()
С
С
      INITIALIZE
     RW=DMAX1(RE,ER)
      AW=DMAX1(AE,0.0D0)
      IC=0
      ACBS=DABS(B-C)
      A=C
      T=A
     FA=F(T)
     T=B
     FB=F(T)
     FC=FA
     KOUNT=2
      FX=DMAX1(DABS(FB),DABS(FC))
С
    1 IF (DABS(FC) .GE. DABS(FB)) GO TO 2
С
     PERFORM INTERCHANGE
     A=B
     FA=FB
     B=C
     FB=FC
      C=A
     FC=FA
С
    2 IF (FB .EQ. 0.0D0) GO TO 11
     CMB=0.5D0*(C-B)
     ACMB=DABS(CMB)
     TOL=RW*DABS(B)+AW
С
С
     TEST STOPPING CRITERION
      IF (ACMB .LE. TOL) GO TO 10
С
С
      CALCULATE NEW ITERATE IMPLICITLY AS B+P/Q
С
      WHERE WE ARRANGE P .GE. 0.
С
      THE IMPLICIT FORM IS USED TO PREVENT OVERFLOW.
      P=(B-A)*FB
      Q=FA-FB
      IF (P .GE. 0.0D0) GO TO 3
      P = -P
      Q = -Q
С
С
      UPDATE A AND CHECK FOR SATISFACTORY REDUCTION
     IN THE SIZE OF OUR BOUNDING INTERVAL.
С
    3 A=B
     FA=FB
      IC=IC+1
      IF (IC .LT. 4) GO TO 4
      IF (8.0D0*ACMB .GE. ACBS) GO TO 6
      IC=0
      ACBS=ACMB
С
С
     TEST FOR TOO SMALL A CHANGE
    4 IF (P .GT. DABS(Q)*TOL) GO TO 5
С
      INCREMENT BY TOLERANCE
С
     B=B+DSIGN(TOL,CMB)
      GO TO 7
С
С
      ROOT OUGHT TO BE BETWEEN B AND (C+B)/2.0D0
    5 IF (P .GE. CMB*Q) GO TO 6
С
      INTERPOLATE
С
```

```
B=B+P/Q
     GO TO 7
С
   6 B=0.5D0*(C+B)
С
    BISECT
С
С
    HAVE COMPLETED COMPUTATION FOR NEW ITERATE B
   7 T=B
     FB=F(T)
     IF (FB .EQ. 0.0D0) GO TO 11
С
     DECIDE WHETHER NEXT STEP IS INTERPOLATION OR EXTRAPOLATION
С
     IF (DSIGN(1.0D0,FB) .NE. DSIGN(1.0D0,FC)) GO TO 8
     C = A
    FC=FA
   8 KOUNT=KOUNT+1
     IF (KOUNT .GT. 500) GO TO 15
     GO TO 1
С
С
С
     FINISHED. PROCESS RESULTS FOR PROPER SETTING OF IFLAG
C
  10 IF (DSIGN(1.0D0,FB) .EQ. DSIGN(1.0D0,FC)) GO TO 13
     IF (DABS(FB) .GT. FX) GO TO 12
     IFLAG = 1
    RETURN
  11 IFLAG = 2
    RETURN
  12 IFLAG = 3
    RETURN
  13 IFLAG = 4
    RETURN
  15 \text{ IFLAG} = 5
    RETURN
    END
    DOUBLE PRECISION FUNCTION BBMACH ()
C-----
C THIS ROUTINE COMPUTES THE UNIT ROUNDOFF OF THE MACHINE IN DOUBLE
C PRECISION. THIS IS DEFINED AS THE SMALLEST POSITIVE MACHINE NUMBER
C U SUCH THAT 1.0D0 + U .NE. 1.0D0 (IN DOUBLE PRECISION).
C-----
    DOUBLE PRECISION U, COMP
    U = 1.0D0
10
    U = U * 0.5 D 0
     COMP = 1.0D0 + U
     IF (COMP .NE. 1.0D0) GO TO 10
    BBMACH = U*2.0D0
    RETURN
C----- END OF FUNCTION BBMACH -----
     END
```

Source Code for Simulated Annealing Optimization Technique

siman.f

```
program siman
    implicit double precision (a-z)
    integer i,j,k,nrxn,nmer,nfiles1,nfiles2,ninner,nouter
```

```
dimension aa(11), aat(11), aao(11)
      dimension aa2(11), aa2t(11), aa2o(11)
      dimension ee(11), eet(11), eeo(11)
c...Read in initial parameters
      open (unit=50, file='param.inp', status='old')
      read (50,*) nrxn
      do 50 j = 1,nrxn
50
         read (50,*) aa2(j),ee(j)
      read (50,*) fli
      read (50,*) dt
      read (50,*) corf
      read (50,*) cdif
      read (50,*) nmer
      read (50,*) nfiles1
      read (50,*) nfiles2
      read (50,*) ninner
      read (50,*) nouter
      read (50,*) a2pert
      read (50,*) epert
      close (50)
c...Calculate temperature and probability parameters
      Ps = 0.5
      Pf = 0.01
      Ts = -1.0/log(Ps)
      Tf = -1.0/log(Pf)
      F = (Tf/Ts) * * (1.0/(nouter - 1.0))
      T = Ts
      DEavg = 1.0
      nchange = 0.0
      perta2 = a2pert*10.0
     perte = epert*80000
      call random_seed()
c...Evaluate and store initial design
     call evaluate(aa2,ee,fli,dt,corf,cdif,nmer,nfiles1,nfiles2,
     &
                    Error,cra,aa)
     Errort = Error
      Erroro = Error
      do 75 i = 1, nrxn
         aa2t(i) = aa2(i)
         aa2o(i) = aa2(i)
         aat(i) = aa(i)
         aao(i) = aa(i)
         eet(i) = ee(i)
75
         eeo(i) = ee(i)
c...Start simulated annealing process
      do 100 i = 1, nouter
         do 200 j = 1, ninner
            do 300 k = 1,nrxn
               call random_number(rnd1)
               call random_number(rnd2)
               aa2(k) = aa2(k)+perta2*(rnd1-0.5)
               ee(k) = ee(k) + perte*(rnd2-0.5)
               if (aa2(k) .gt. 10.0) aa2(k) = 10.0
if (aa2(k) .lt. 0.0) aa2(k) = 0.0
               if (ee(k) .gt. 100000) ee(k) = 100000
               if (ee(k) . lt. 20000) ee(k) = 20000
300
            continue
            open (unit=23, file='ndes.out', status='unknown')
            do 750 k = 1,nrxn
750
               write (23,1000) aa2(k),ee(k),aa(k)
            close (23)
            call evaluate(aa2,ee,fli,dt,corf,cdif,nmer,nfiles1,nfiles2,
     &
                           Error1,cra,aa)
```

```
if (Error1 .le. Erroro) then
               do 350 \text{ k} = 1, \text{nrxn}
                   aa2o(k) = aa2(k)
                   aao(k) = aa(k)
350
                   eeo(k) = ee(k)
               Erroro = Error1
            end if
            if (Error1 .le. Error) then
               do 400 \text{ k} = 1, \text{nrxn}
                   aa2t(k) = aa2(k)
                   aat(k) = aa(k)
400
                   eet(k) = ee(k)
               DE = Error-Error1
               Error = Error1
               Errort = Error1
               DEavg = (DEavg*nchange+DE)/(nchange+1.0)
               nchange = nchange+1.0
            else
               call random_number(prob)
               DE = Error1-Error
               if (nchange .eq. 0.0) then
                   prot = \exp(-1.0/T)
               else
                  prot = exp(-DE/(DEavg*T))
               end if
               if (prob .le. prot) then
                   do 500 k = 1,nrxn
                      aa2t(k) = aa2(k)
                      aat(k) = aa(k)
500
                      eet(k) = ee(k)
                   DE = Error-Error1
                   Error = Error1
                   Errort = Error1
                   DEavg = (DEavg*nchange+DE)/(nchange+1.0)
                   nchange = nchange+1.0
               else
                   do 600 \text{ k} = 1, \text{nrxn}
                      aa2(k) = aa2t(k)
600
                      ee(k) = eet(k)
               end if
            end if
200
         continue
         T = F*T
         open (unit=19, file='prog.out', status='unknown')
         write (19,*) "Cycle ",i," completed"
         write (19,*) "Current Error
                                          Best Error"
         write (19,2000) Errort, Erroro
         close (19)
         open (unit=20, file='sum.out', status='unknown')
         write (20,*) "Cycle ",i," completed"
         write (20,*) "Current Error
                                         Best Error"
         write (20,2000) Errort, Erroro
         open (unit=21, file='cdes.out', status='unknown')
         write (21,2000) Errort
         do 700 j = 1,nrxn
700
            write (21,1000) aa2t(j),eet(j),aat(j)
         close (21)
         open (unit=22, file='bdes.out', status='unknown')
         write (22,2000) Erroro
         do 800 j = 1, nrxn
800
            write (22,1000) aa2o(j),eeo(j),aao(j)
         close (22)
100
      continue
```

```
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```

```
1000 format(' ',f8.4,lx,f6.0,lx,(1P,g11.4))
2000 format(' ',3x,f6.2,10x,f6.2)
end
```

evaluate.f

```
subroutine evaluate(aa2,ee,fli,dt,corf,hcor,nnmer,nn1,nn2,
                          Error, cra, aa)
     &
     implicit double precision (a-z)
      integer i,j,k,nin,nfiles1,nfiles2,nmer,ndata,nnmer,nn1,nn2,nrxn
     parameter (nrxn = 11)
      character fn*8, name*8, name2*8
      dimension fma(100),dfma(100),tcal(100),ee(nrxn),aa(nrxn),aa2(nrxn)
     dimension tt(2000),dd(2000)
c...Make sure inputs are integers
     nfiles1 = int(nn1)
     nfiles2 = int(nn2)
     nmer = int(nnmer)
c...Calculate preexponential factors
      do 50 i = 1, nrxn
         aa(i) = 10.d0**aa2(i)*dexp(ee(i)/2000.d0)
50
c...compute intermediate functions
     Error = 0.D0
      cra = 0.D0
      err = 0.D0
      do 100 i = 40+nfiles1,40+nfiles2
         fn="input."
         call fname(fn,6,i-40,name)
        nin = i
         err = 0.D0
         call mtpuf2(nin,name,aa,ee,fli,dt,corf,hcor,nmer,fma,tcal,err)
         fn="data."
         call fname(fn,5,i-40,name2)
         open (i+40,file=name2,status='old')
c...Read in data versus time
         read (i+40,*) ndata
         do 200 j = 1,ndata
200
            read (i+40,*) tt(j),dd(j)
         sume = 0.D0
         do 300 \text{ k} = 1,100
            dfma(k) = tfun(tcal(k),ndata,tt,dd)
300
            sume = sume+dsqrt((fma(k)-dfma(k))**2)
         Error = Error+sume
         cra = cra+err
         close (i+40)
100
         continue
     return
      end
```

fname.f

```
SUBROUTINE FNAME(FN,LENGTH,N,NAME)

CHARACTER FN*8,NAME*8

CHARACTER*1 L1,L2

INTEGER N,I1,I2,LENGTH

CHARACTER DIGITTS*10

DIGITTS = '1234567890'

I1 = N/10

I2 = (N-I1*10)
```

```
IF (I1.EQ.0) THEN
L1 = '0'
ELSE
L1 = DIGITTS(I1:I1)
END IF
IF (I2.EQ.0) THEN
L2 = '0'
ELSE
L2 = DIGITTS(I2:I2)
END IF
NAME = FN(1:LENGTH)//L1//L2
return
end
```

init2.f

```
subroutine init2(nin,name,nmer)
C23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x12
C-----C
C This subroutine initializes the parameters used in the CPUF program
C-----C
implicit double precision (a-h,o-z)
      parameter (nrxn=11)
      parameter (neq1 = 16, neq2 = 12, maxt = 4000)
      character*80 csay
      character name*8
      double precision L10, L20, L30, L40, mw, mwinf, mwinert, mp0
common /cdbl1/ CO20,CPN0,D10,D20,D30,D40,D50,D60,S10,S20,TDI0,TDA0
      common /cdbl2/ L10,L20,L30,L40
      common /cdbl3/ mw(neq1),mwinf,mwinert
      common /cdbl4/ a(nrxn),e(nrxn),esig
      common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
      common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
      common /cdbl7/ mp0,Vol,conf,fli,fac
      common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,hbas
      common /cint1/ iprint,ntmax
      common /cint2/ nnmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
      common /cttime/ tim(maxt),tem(maxt),timax,ntim
data half,one/0.5D0,1.0D0/
     nnmer = nmer
С-----С
C Open input and output files
C-----C
     open (unit = nin,file = name, status = 'old')
C-----C
C Begin reading data from cpuf.in
C-----C
     read (nin,*) nsay
      do 100 n = 1,nsay
100
       read (nin,1000) csay
C average coordination number
     read (nin,*) sigp1
C Number of bridge types
      read (nin,*) nbrg
C Initial urethane bridge population and molecular weight
      read (nin,*) L10,mw(1)
C Initial aminourethane bridge population and molecular weight
     read (nin,*) L20,mw(2)
```

```
C Initial diamine bridge population and molecular weight
      read (nin,*) L30,mw(3)
C Initial adipate bridge population and molecular weight
     read (nin,*) L40,mw(4)
C Number of side chain types
     read (nin,*) nsch
C Initial isocyanate side chain and molecular weight
     read (nin,*) D10,mw(5)
C Initial OH side chain and molecular weight
      read (nin,*) D20,mw(6)
C Initial amino urethane side chain and molecular weight
     read (nin,*) D30,mw(7)
C Initial diamine side chain and molecular weight
     read (nin,*) D40,mw(8)
C Initial CH2 radical side chain and molecular weight
     read (nin,*) D50,mw(9)
C Initial CH2O radical side chain and molecular weight
     read (nin,*) D60,mw(10)
C Number of site types
     read (nin,*) nsit
C Site 1 population and molecular weight (TMP)
     read (nin,*) S10,mw(11)
C Site 2 population and molecular weight (DEG)
     read (nin,*) S20,mw(12)
C Number of light molecule types
     read (nin,*) ngas
C Initial TDI fraction and molecular weight
      read (nin,*) TDI0,mw(13)
C Initial TDA fraction and molecular weight
     read (nin,*) TDA0,mw(14)
C Initial CPN fraction and molecular weight
     read (nin,*) CPN0,mw(15)
C Initial CO2 fraction and molecular weight
     read (nin,*) CO20,mw(16)
c Calculate variables for convenience
     ncom = nbrg+nsch+nsit
     nreac = ncom+ngas
     ntot = nreac+nmer+2
     ntot2 = ngas+nmer+2
C Molecular weight of infinite polymer, g/mol
     read (nin,*) mwinf
C Molecular weight and flowrate of inert atmosphere, g/mol, cc/sec
     read (nin,*) fli,mwinert
C Mass and density of initial polymer (mers, infinite matrix
C and light molecules, g, g/cm3
     read (nin,*) mp0,rhos
C Volume in interest and confinement, cm3, unitless
     read (nin,*) Vol,conf
C Ratio of specific heats and ambient pressure, unitless, atm, m
     read (nin,*) gamma,pamb
C Diameter and coefficient of orifice, cm and unitless
     read (nin,*) dorf,corf
C Basket height, cm
     read (nin,*) hbas
C Pressure in atmospheres
     read (nin,*) press
C Read in critical pressures, critical temperatures and accentric factors
      do 200 i = 1, ngas
        read (nin,*) tc(i+nmer),pc(i+nmer),omega(i+nmer)
200
c Mer sizes
     read (nin,*) tc(1),pc(1),omega(1)
     read (nin,*) tc(2),pc(2),omega(2)
     read (nin,*) tc(3),pc(3),omega(3)
```

```
C As a first approx., set all n-mers above a 3-mer to the 3-mer values
      do 250 i = 4,nmer
         tc(i) = tc(3)
         pc(i) = pc(3)
250
         omega(i) = omega(3)
c Infinite Matrix
     read (nin,*) tc(ntot2-1),pc(ntot2-1),omega(ntot2-1)
c Inert gas
     read (nin,*) tc(ntot2),pc(ntot2),omega(ntot2)
C Time step for calculation
     read (nin,*) timax
C Input temperature history
     read (nin,*) ntim
      do 300 i = 1,ntim
300
        read (nin,*) tim(i),tem(i)
c Close file
     close (nin)
C Initialize variables
     rhol = rhos
      sig = sigp1-one
      siginv = one/sig
     sigp12 = sigp1/2.D0
     return
1000 format(1a80)
2000 format(15)
      end
```

mtpuf2.f

```
subroutine mtpuf2(nin,name,aa,ee,ffli,dtt,ccorf,hcor,nnmer, fma,tcal,err)
C23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123
C------C
C The Mass Transfer PolyUrethane Foam (MTPUF) decomposition model is an
C extended version of the CPUF model referenced in
С
    (1) Hobbs, M. L., Erickson, K. E., and Chu, T. Y., "Modeling Decomposition
С
С
          of Unconfined Rigid Polyurethane Foam," Polymer Degradation and
С
          Stability, (1999).
С
С
   The primary difference in the PUF model and the CPUF model is the
   in regards to the kinetic scheme. The PUF mechanism is based on a
С
С
   retrograde reaction followed by the formation of a secondary polymer
   which is stable below about 350 C. This mechanism can be considered a
С
С
   generalization of the CPD model developed by Fletcher et al.:
С
                             /--> C1 + G1
L* - /--> G2
\<--> d*-- /--> C2 + G4
\--> 2L --
С
  11 "species"
С
     9 reactions
С
С
                                                 -G3
                                                              \<--> d --> G5
С
С
  The MTPUF model is based on Erickson et al. experiments and considers
С
C four different bridge types, 6 side chain types, 4 light molecule types,
C and two sites types:
C L1 [=] urethane bridge
                                               D1 [=] isocyanate side chain
C L2 [=] aminourethane bridge
                                               D2 [=] OH side chain
C L3 [=] diamine bridge
                                               D3 [=] aminourethane side chain
                                               D4 [=] diamine side chain
C L4 [=] adipate bridge
                                               D5 [=] CH2 radical side chain
C
C TDI [=] toluene diisocyanate D6 [=] CH2O radical side chain
C TDA [=] toluene diamine
```

```
C CPN [=] cyclopentanone
                           S1 [=] TMP site
C CO2 [=] carbon dioxide
                            S2 [=] DEG site
С
С
                    (1 \ 2)
                               (3\4)
C 16 "species"
                 L1 <--> D1 + D2 <--> TDI + 2 D2
C 11 reactions
                   \ (5) (6\7)
                    \--> L2 <--> D2 + D3
С
                         \ (8) (9)
С
                    -C02
                                           (10)
С
                           \--> L3 --> D4 + D5 --> TDA + 2 D5
С
                           -CO2
С
                   (11)
С
                 L4 --> D5 + CPN + CO2 + D6
С
С
            ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
 v(1) = L1
C y(5) = D1 ; y(6) = D2 ; y(7) = D3 ; y(8) = D4
C y(9) = D5 ; y(10) = D6 ; y(11) = S1 ; y(12) = S2
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
С
C The initial polymer structure is assumed to be composed of two
C bridge types (the urethane and adipate bridges) and two different
C site types (the trimethylol propane, and diethyleneglycol).
C-----
                                  -----C
implicit double precision (a-h,o-z)
     parameter (neq1 = 16, neq2 = 12, maxt = 4000, nrxn = 11)
     parameter (lrw = 250 + neg1 * (10 + neg1), liw = 56 + neg1)
     character name*8
     dimension rwork(lrw),iwork(liw),info(15)
     double precision L10, L20, L30, L40, lsys0, mw, mwinf, mwinert, mp0
     double precision ms0,ml0,mg0,mtot,mwv,mwf,ms,ml,mg,mi
     double precision y(neq1), yold(neq1)
     double precision w(neq2),ft(neq2),mt(neq2),ywt(neq2),twout(neq2)
     double precision aa(nrxn),ee(nrxn),fma(100),tcal(100)
     external func
     external rpcrit
C. . .COMMON BLOCK AREA. . . . . . . . .
     common /cdbl1/ CO20,CPN0,D10,D20,D30,D40,D50,D60,S10,S20,TD10,TDA0
     common /cdbl2/ L10,L20,L30,L40
     common /cdbl3/ mw(neq1),mwinf,mwinert
     common /cdbl4/ a(nrxn),e(nrxn),esig
     common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
     common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
     common /cdbl7/ mp0,Vol,conf,fli,fac
     common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,hbas
     common /cint1/ iprint,ntmax
     common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
     common /cttime/ tim(maxt),tem(maxt),timax,ntim
data zero, one, two /0.D0, 1.D0, 2.D0/
     data half, small /0.5D0, 1.D-20/
c...[Rq] = cm3*atm/mol/K
     data Rg /82.057841D0/
C-----C
C Call init to initialize parameters and read input files
С------С
     nmer = nnmer
     call init2(nin,name,nmer)
     do 10 i = 1,nrxn
10
      a(i) = aa(i)
     do 20 i = 1, nrxn
20
      e(i) = ee(i)
     esig = 0.
     fli = ffli
```

```
dt = dtt
   mwinf = 8000.
   corf = ccorf
   hbas = hbas*hcor
   ntmax = idint(timax/dt)
   idat = idint(timax/100.d0/dt)
   index = 1
   err = zero
C-----C
 Initialize solver variables
C------^
   call sinit(info,atol,rtol)
C-----C
C Calculate initial values
C-----C
   fmas = one
C-----C
C y(1) = L1 ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
C y(5) = D1 ; y(6) = D2 ; y(7) = D3 ; y(8) = D4
C y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
                                   -----C
C-
   y(1) = L10
   y(2) = L20
   y(3) = L30
   y(4) = L40
   y(5) = D10
   y(6) = D20
   y(7) = D30
   y(8) = D40
   y(9) = D50
   y(10) = D60
   y(11) = S10
   y(12) = S20
   y(13) = TDI0
   y(14) = TDA0
   y(15) = CPN0
   y(16) = CO20
   psys0 = L10+L20+L30+L40
   psys = psys0
   lsys0 = CO20+CPN0+TDA0+TDI0
C-----C
C Calculate p critical
C-----C
   p0 = zero
   pl = siginv
   call zeroin(rpcrit,p0,p1,rez,aez,iflag)
   pcrit = p0
C-----C
C Percolation lattice statistics of initial conditons
C-----C
   call mwavq(y,fsit,fbrq,fsch,flm)
   call perk(y,psys0,ft,mt,ftinf,totmas)
   totmasp = totmas+sigp12*flm*lsys0
С-----С
C Add the molecular weight of the gases, infinite matrix and inert
C-----C
   do 25 i = 1, ngas
25
    mt(i+nmer) = mw(ncom+i)
   mt(ntot2-1) = mwinf
   mt(ntot2) = mwinert
C-----C
C Calculate the masses of the mers and the infinite matrix
```

```
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```

```
C-----C
   do 50 i = 1, nmer
50
    w(i) = ft(i)*mp0*totmas/totmasp
   w(ntot2-1) = ftinf*mp0*totmas/totmasp
C-----C
C Calculate the masses of the light molecules from the initial populations
C-----C
    fac = sigp12*mp0/totmasp
    do 75 i = 1, ngas
75
    w(i+nmer) = y(ncom+i)*mt(i+nmer)*fac
C-----C
C Calculate the amount of inert gas to be added to get
C the correct pressure
C-----C
   count = zero
    vs0 = mp0/rhos
    vq0 = Vol-vs0
    tp0 = tfun(zero,ntim,tim,tem)
C Guess all gas is inert
   w(ntot2) = press*vg0/Rg/tp0*mt(ntot2)
90
   call phases(w,mt,tp0,press,mg0,ml0,ms0,mwv,vg0,comp,ywt)
   press1 = mg0*rg*tp0*comp/vg0/mwv
C-----C
C Check to see if the pressure matches with relative error test (1%)
С-----С
    rperror = (press1-press)/press
    if (abs(rperror) .ge. 0.0001 .and. count .le. 100.D0) then
      w(ntot2) = w(ntot2)*(one-rperror)
      count = count+one
      goto 90
    end if
    do 95 i = 1,ntot2
95
   twout(i) = zero
C-----C
C Begin solvers Do loop
C------C
   time = zero
    tout = zero
   do 100 iii = 1, ntmax
C-----C
C Call DDEBDF y(1) = L1; y(2) = L2; y(3) = L3; y(4) = L4
 to integrate: y(5) = D1; y(6) = D2; y(7) = D3; y(8) = D4
С
С
           y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
С
           y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
C-----
                  _____
     do 150 i = 1, neq1
150
       yold(i) = y(i)
      if (fmas .lt. 0.0001) then
       time = time+dt
        goto 200
      end if
      conv = zero
      tout = time+dt
300
      call ddebdf (func,neq1,time,y,tout,info,rtol,atol,idid,
              rwork,lrw,iwork,liw,rpar,ipar,jac)
200
      tp = tfun(time,ntim,tim,tem)
      info(1) = 0
      if (idid.lt.0) then
        conv = one
      end if
     do 250 i = 1,neq1
250
     y(i) = max(y(i), zero)
С-----
                          -----^
```

```
C Calculate mass (mas) and molecular weight (mt) of gas species and mers
C-----C
    call popmas(y,yold,psys,w,mt)
С-----С
C Calculate flow effects (with flash included)
С-----С
     call flow(y,w,mt,tp,ms,ml,mg,mi,psys,twout)
      fmas = (ms+ml+mq-mi)/mp0
      totm = mg+ms+ml
      if (mod(iii,idat).eq. 0 .and. index .le. 100) then
        fma(index) = fmas+conv
        tcal(index) = time
        err = err+conv
        index = index+1
      end if
100
   continue
   end
```

Source Code for Totally Confined Experiments

mtpuf3.f

```
program mtpuf3
С-----С
C The Mass Transfer PolyUrethane Foam (MTPUF) decomposition model is an
C extended version of the CPUF model referenced in
С
С
  (1) Hobbs, M. L., Erickson, K. E., and Chu, T. Y., "Modeling Decomposition
      of Unconfined Rigid Polyurethane Foam," Polymer Degradation and
С
С
      Stability, (1999).
С
  The primary difference in the PUF model and the CPUF model is the
С
C in regards to the kinetic scheme. The PUF mechanism is based on a
C retrograde reaction followed by the formation of a secondary polymer
C which is stable below about 350 C. This mechanism can be considered a
C generalization of the CPD model developed by Fletcher et al.:
С
                      /--> Cl + Gl
C 11 "species"
                  L* - /--> G2
\<--> d*-- /--> C2 + G4
С
  9 reactions
С
                               \--> 2L --
С
С
                                -G3
                                         \<--> d --> G5
С
С
  The MTPUF model is based on Erickson et al. experiments and considers
  four different bridge types, 6 side chain types, 4 light molecule types,
С
С
  and two sites types:
C
C L1 [=] urethane bridge
                             D1 [=] isocyanate side chain
                            D2 [=] OH side chain
C L2 [=] aminourethane bridge
C L3 [=] diamine bridge
                             D3 [=] aminourethane side chain
                             D4 [=] diamine side chain
C L4 [=] adipate bridge
                              D5 [=] CH2 radical side chain
С
C TDI [=] toluene diisocyanate D6 [=] CH2O radical side chain
C TDA [=] toluene diamine
C CPN [=] cyclopentanone S1 [=] TMP site
C CO2 [=] carbon dioxide S2 [=] DEG site
С
```

```
С
                  (1 \ 2)
                         (3\4)
               L1 <--> D1 + D2 <--> TDI + 2 D2
C 16 "species"
C 11 reactions
                 \ (5)
                        (6\7)
                  \--> L2 <--> D2 + D3
С
С
                  -CO2 \ (8) (9)
                                     (10)
                        \--> L3 --> D4 + D5 --> TDA + 2 D5
С
С
                        -CO2
С
                (11)
С
               L4 --> D5 + CPN + CO2 + D6
C
С
  y(1) = L1
          ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
          i y(6) = D2 \quad i y(7) = D3 \quad i y(8)
С
  y(5) = D1
                                      = D4
 y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
С
С
 y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
C
C The initial polymer structure is assumed to be composed of two
C bridge types (the urethane and adipate bridges) and two different
C site types (the trimethylol propane, and diethyleneglycol).
C-----C
implicit double precision (a-h,o-z)
    parameter (neq1 = 16, neq2 = 12, maxt = 4000)
    parameter (lrw = 250 + neg1 * (10 + neg1), liw = 56 + neg1)
    dimension rwork(lrw), iwork(liw), info(15)
    double precision L10,L20,L30,L40,lsys0,mw,mwinf,mwinert,mp0
    double precision ms0,ml0,mg0,mtot,mwv,mwf,ms,ml,mg,mi
    double precision y(neq1),yold(neq1)
    double precision w(neq2),ft(neq2),mt(neq2),ywt(neq2),twout(neq2)
    external func
    external rpcrit
C. . . COMMON BLOCK AREA. . . . . . . .
    common /cdbl1/ CO20,CPN0,D10,D20,D30,D40,D50,D60,S10,S20,TD10,TDA0
    common /cdbl2/ L10,L20,L30,L40
    common /cdbl3/ mw(neq1),mwinf,mwinert
    common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
    common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
    common /cdbl7/ mp0,Vol,conf,fli,fac
    common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,hbas
    common /cint1/ iprint,ntmax
    common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
    common /cttime/ tim(maxt),tem(maxt),pres(maxt),timax,ntim
data zero, one, two /0.D0,1.D0,2.D0/
    data half,small /0.5D0,1.D-20/
c...[Rg] = cm3*atm/mol/K
    data Rg,pi /82.057841D0,3.1415926D0/
С-----С
C Call init3 to initialize parameters and read input files
С-----С
    call init3
C-----C
  Initialize solver variables
С
C-----C
    call sinit(info,atol,rtol)
C-----C
С
 Calculate initial values
С-----С
   fmas = one
C-----C
C y(1) = L1 ; y(2) = L2 ; y(3) = L3 ; y(4) = L4
C y(5) = D1 ; y(6) = D2 ; y(7) = D3 ; y(8) = D4
C y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
C y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
```

```
C-----C
   y(1) = L10
   y(2) = L20
   y(3) = L30
   y(4) = L40
   y(5) = D10
   y(6) = D20
   y(7) = D30
   y(8) = D40
   y(9) = D50
   y(10) = D60
   y(11) = S10
   y(12) = S20
   y(13) = TDI0
   y(14) = TDA0
   y(15) = CPN0
   y(16) = CO20
   psys0 = L10+L20+L30+L40
   psys = psys0
   lsys0 = CO20+CPN0+TDA0+TDI0
C-----C
C Calculate p critical
C-----C
   p0 = zero
   pl = siginv
   call zeroin(rpcrit,p0,p1,rez,aez,iflag)
   pcrit = p0
C-----C
C Percolation lattice statistics of initial conditons
С-----С
   call mwavq(y,fsit,fbrq,fsch,flm)
   call perk(y,psys0,ft,mt,ftinf,totmas)
   totmasp = totmas+sigp12*flm*lsys0
С-----С
C Add the molecular weight of the gases, infinite matrix and inert
C-----C
   do 25 i = 1, ngas
25
    mt(i+nmer) = mw(ncom+i)
   mt(ntot2-1) = mwinf
   mt(ntot2) = mwinert
С-----С
C Calculate the masses of the mers and the infinite matrix
C-----C
   do 50 i = 1, nmer
50
    w(i) = ft(i)*mp0*totmas/totmasp
   w(ntot2-1) = ftinf*mp0*totmas/totmasp
C-----C
C Calculate the masses of the light molecules from the initial populations
С-----С
   fac = sigp12*mp0/totmasp
   do 75 i = 1, ngas
75
    w(i+nmer) = y(ncom+i)*mt(i+nmer)*fac
C-----C
C Calculate the amount of inert gas to be added to get
C the correct pressure
С-----С
   count = zero
   vs0 = mp0/rhos
   vq0 = Vol-vs0
   tp0 = tfun(zero,ntim,tim,tem)
   press = tfun(zero,ntim,tim,pres)
C Guess all gas is inert
   w(ntot2) = press*vg0/Rg/tp0*mt(ntot2)
```

```
90
    call phases(w,mt,tp0,press,mg0,ml0,ms0,mwv,vg0,comp,ywt)
    press1 = mg0*rg*tp0*comp/vg0/mwv
C----
   -----^
C Check to see if the pressure matches with relative error test (1%)
С-----С
    rperror = (press1-press)/press
    if (abs(rperror) .ge. 0.0001 .and. count .le. 100.D0) then
      w(ntot2) = w(ntot2)*(one-rperror)
      count = count+one
      goto 90
    end if
    do 95 i = 1,ntot2
95
    twout(i) = zero
C-----C
C Begin solvers Do loop
C-----C
    time = zero
    tout = zero
    do 100 iii = 1, ntmax
C-----C
 Call DDEBDF y(1) = L1; y(2) = L2; y(3) = L3; y(4) = L4
to integrate: y(5) = D1; y(6) = D2; y(7) = D3; y(8) = D4
y(9) = D5; y(10) = D6; y(11) = S1; y(12) = S2
С
C
C
C
            y(13) = TDI ; y(14) = TDA ; y(15) = CPN ; y(16) = CO2
С-----С
      do 150 i = 1, neq1
        yold(i) = y(i)
150
      if (fmas .lt. 0.0001) then
         time = time+dt
         goto 200
      end if
      tout = time+dt
      call ddebdf (func,neq1,time,y,tout,info,rtol,atol,idid,
300
                rwork,lrw,iwork,liw,rpar,ipar,jac)
   &
200
      tp = tfun(time,ntim,tim,tem)
      press = tfun(time,ntim,tim,pres)
      info(1) = 0
      if (idid.lt.0) then
         call error (idid,'cpuf.f',1,rwork,info)
      end if
      do 250 i = 1,neq1
250
       y(i) = max(y(i), zero)
C-----C
C Calculate mass (mas) and molecular weight (mt) of gas species and mers
C-----C
      call popmas(y,yold,psys,w,mt)
С-----С
C Calculate flow effects (with flash included)
С-----С
      call flow3(y,w,mt,tp,ms,ml,mg,mi,psys,twout,volume)
      fmas = (ms+ml+mg-mi)/mp0
      totm = mg+ms+ml
      csa = pi*(dorf/two)**two
      convcmin = .3937
      disp = (volume/csa)*convcmin
      if (mod(iii, iprint).eq.0) then
         write(26,3000)time/60.,tp-273.15,press,Volume,disp
      end if
100
    continue
    close (26)
1000 format(2x, f6.2, 2x, 17(1x, f7.5))
2000 format(2x, f6.2, 2x, 12(1x, e10.3))
3000 format(2x,f6.2,3x,f6.2,2x,7(1x,f8.5))
```

end

init3.f

```
subroutine init3
C23456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x123456789x12
С-----С
C This subroutine initializes the parameters used in the CPUF program
С-----С
implicit double precision (a-h,o-z)
      parameter (nin=10, nrxn=11)
      parameter (neg1 = 16, neg2 = 12, maxt = 4000)
      character*80 csay
      double precision L10, L20, L30, L40, mw, mwinf, mwinert, mp0
C. . . COMMON BLOCK AREA. . . . .
      common /cdbl1/ CO20,CPN0,D10,D20,D30,D40,D50,D60,S10,S20,TD10,TDA0
      common /cdbl2/ L10,L20,L30,L40
      common /cdbl3/ mw(neq1),mwinf,mwinert
      common /cdbl4/ a(nrxn),e(nrxn),esig
      common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
      common /cdbl6/ tc(neq2),pc(neq2),omega(neq2)
      common /cdbl7/ mp0,Vol,conf,fli,fac
      common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,hbas
      common /cint1/ iprint,ntmax
      common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
      common /cttime/ tim(maxt),tem(maxt),pres(maxt),timax,ntim
data half,one/0.5D0,1.0D0/
C-----C
C Open input and output files
C-----C
      open (unit = nin,file = 'mtpuf.in', status = 'old')
      open (unit = 26, file = 'outsol',status = 'unknown')
     write(26,5000)
                      -----
C-----
C Begin reading data from cpuf.in
С-----С
      read (nin,*) nsay
      do 100 n = 1, nsay
100
       read (nin,1000) csay
C average coordination number
      read (nin,*) sigp1
C Number of bridge types
      read (nin,*) nbrg
C Initial urethane bridge population and molecular weight
      read (nin,*) L10,mw(1)
C Initial aminourethane bridge population and molecular weight
      read (nin,*) L20,mw(2)
C Initial diamine bridge population and molecular weight
      read (nin,*) L30,mw(3)
C Initial adipate bridge population and molecular weight
      read (nin,*) L40,mw(4)
C Number of side chain types
      read (nin,*) nsch
C Initial isocyanate side chain and molecular weight
      read (nin,*) D10,mw(5)
C Initial OH side chain and molecular weight
      read (nin,*) D20,mw(6)
C Initial amino urethane side chain and molecular weight
      read (nin,*) D30,mw(7)
```

```
C Initial diamine side chain and molecular weight
      read (nin,*) D40,mw(8)
C Initial CH2 radical side chain and molecular weight
      read (nin,*) D50,mw(9)
C Initial CH2O radical side chain and molecular weight
      read (nin,*) D60,mw(10)
C Number of site types
     read (nin,*) nsit
C Site 1 population and molecular weight (TMP)
      read (nin,*) S10,mw(11)
C Site 2 population and molecular weight (DEG)
     read (nin,*) S20,mw(12)
C Number of light molecule types
     read (nin,*) ngas
C Initial TDI fraction and molecular weight
     read (nin,*) TDI0,mw(13)
C Initial TDA fraction and molecular weight
      read (nin,*) TDA0,mw(14)
C Initial CPN fraction and molecular weight
      read (nin,*) CPN0,mw(15)
C Initial CO2 fraction and molecular weight
      read (nin,*) CO20,mw(16)
C Number of mer size to be considered in the calculations
      read (nin,*) nmer
c Calculate variables for convenience
     ncom = nbrg+nsch+nsit
     nreac = ncom+ngas
     ntot = nreac+nmer+2
     ntot2 = ngas+nmer+2
C Molecular weight of infinite polymer, g/mol
     read (nin,*) mwinf
C Molecular weight and flowrate of inert atmosphere, g/sec, g/mol
     read (nin,*) fli,mwinert
C Mass and density of initial polymer (mers, infinite matrix
C and light molecules), g, g/cm3 \,
     read (nin,*) mp0,rhos
C Volume in interest and confinement, cm3, unitless
      read (nin,*) Vol,conf
C Ratio of specific heats and ambient pressure, unitless, atm
      read (nin,*) gamma,pamb
C Diameter and coefficient of orifice, cm and unitless
     read (nin,*) dorf,corf
C Basket height, cm
     read (nin,*) hbas
C Kinetic coefficients
     read (nin, *) (a(i), i = 1, 4)
      read (nin, *) (a(i), i = 5, 8)
      read (nin, *) (a(i), i = 9, nrxn)
     read (nin, *) (e(i), i = 1, 4)
     read (nin, *) (e(i), i = 5, 8)
      read (nin, *) (e(i), i = 9, nrxn)
      read (nin,*) esig
C Pressure in atmospheres
      read (nin,*) press
C Read in critical pressures, critical temperatures and accentric factors
      do 200 i = 1,ngas
200
         read (nin,*) tc(i+nmer),pc(i+nmer),omega(i+nmer)
c Mer sizes
      read (nin, *) tc(1), pc(1), omega(1)
      read (nin, *) tc(2),pc(2),omega(2)
      read (nin, *) tc(3),pc(3),omega(3)
C As a first approx., set all n-mers above a 3-mer to the 3-mer values
      do 250 i = 4, nmer
```

```
tc(i) = tc(3)
         pc(i) = pc(3)
250
         omega(i) = omega(3)
c Infinite Matrix
      read (nin,*) tc(ntot2-1),pc(ntot2-1),omega(ntot2-1)
c Inert gas
      read (nin,*) tc(ntot2),pc(ntot2),omega(ntot2)
C Time step for calculation
      read (nin,*) dt0,iprint,dtmax
      read (nin,*) timax
C Input temperature history
      read (nin,*) ntim
      do 300 i = 1,ntim
         read (nin,*) tim(i),tem(i),pres(i)
300
C Initialize variables
      rhol = rhos
      sig = sigpl-one
      siginv = one/sig
      siqp12 = siqp1/2.D0
      ntmax = idint(timax/dt0)
      dt = dmin1(dt0, dtmax)
      return
1000 format(1a80)
2000 format(15)
5000 format(' time (m) temp (C) Vol (cm3) Displacement (in)')
      end
```

flow3.f

```
subroutine flow3(y,w,mt,tp,ms,ml,mg,mi,p,twout,volume)
C-----C
C This program updates the overall mass fractions, mass, pressure and
C gas mass fraction to account for flow/confinement.
C-----
                                    ----C
implicit double precision (a-h,o-z)
   parameter (neq1 = 16, neq2 = 12)
   double precision ms,ml,mg,mwv,mp0,mi
   double precision y(neq1),twout(neq2)
   double precision w(neq2),mt(neq2),win(neq2),wout(neq2),ywt(neq2)
common /cdbl5/ dt,dt0,dtmax,press,pcrit,sig,sigp1,siginv,sigp12
   common /cdbl7/ mp0,Vol,conf,fli,fac
   common /cdbl8/ rhos,rhol,gamma,pamb,dorf,corf,cdif
   common /cint2/ nmer,nbrg,nsch,nsit,ngas,ncom,nreac,ntot,ntot2
data zero, one, two /0.D0, 1.D0, 2.D0/
   data half,small /0.5D0,1.D-20/
c...[Rg] = cm3*atm/mol/K
   data Rg /82.057841D0/
C-----C
C This program updates the overall mass fractions, mass, pressure and
C gas mass fraction to account for flow/confinement.
C-----
                                   -----C
C-----C
C Calculate the different phases
С------С
   call phases(w,mt,tp,press,mg,ml,ms,mwv,vg,comp,ywt)
   Volume = mg*rg*tp/mwv/press*comp+ml/rhol+ms/rhos
   return
   end
```