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Activated Carbon and Cherry Flavor  
Recovery From Cherry Pits

presented by

Aaron D. Soule

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**STUDIES OF GAS ADSORPTION ON ACTIVATED CARBON AND CHERRY  
FLAVOR RECOVERY FROM CHERRY PITS**

**By**

**Aaron D. Soule**

**A THESIS**

**Submitted to  
Michigan State University  
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## ABSTRACT

### STUDIES OF GAS ADSORPTION ON ACTIVATED CARBON AND CHERRY FLAVOR RECOVERY FROM CHERRY PITS

By

Aaron D. Soule

This thesis considers two thrusts. The first thrust considers the application of adsorption, as well as some other separations processes, to the recovery of natural cherry flavoring from cherry pits. Some benchmark work has been established relating to the filtration, extraction, and distillation methods presented here. Each experimental apparatus is presented in detail. Some adsorption data is also presented pertaining to benzaldehyde and benzyl alcohol on synthetic resins. It was found that benzaldehyde adsorbs more strongly in each case with the two aromatics showing signs of competitive adsorption.

The second thrust of this thesis involves mathematical modeling of gas adsorption on activated carbon. Both mixtures and pure systems will be discussed. The Simplified Local Density (SLD) model treats the carbon surface area as slits with some effective slit width. Fluid-solid interaction parameters are used to calculate density profiles across the slit, thus, yielding an adsorbed amount upon integration over the slit width. The ESD (Elliott-Suresh-Donohue) equation of state is used to calculate local compositions, pressures, and fugacities. This method of adsorption prediction works well for gases such as methane and ethylene. It also works well for ethylene-methane and ethane-methane binary mixtures. However, for a CO<sub>2</sub>-toluene fit, the model can only demonstrate qualitative properties at this point in time.

**I dedicate this finished product to my family for their unending support and love.**

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---

Regards to the friends who have come and gone over the years. You will see me again.

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Special thanks to Cassandra Smith for her contributions in chapter 3.

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Credit goes to Greg Donath and Ryoko Yamasaki for assisting in the adsorption runs and issues related to the GC.

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## NOMENCLATURE

A - surface area per unit weight of adsorbent  
a - Peng- Robinson attractive energy parameter  
b - ESD size parameter  
c - shape factor for ESD repulsive term  
*Eta* - distance from first wall in slit model/fluid-solid diameter  
f - fugacity  
H - distance from carbon center to carbon center across slit  
k - Boltzmann's constant  
P - pressure  
R - gas constant  
T - temperature  
Xi - distance from second wall in slit/fluid-solid diameter  
Y - ESD attractive energy parameter  
z - direction of finite length  
Z - compressibility factor

### *Greek*

$\alpha$  - spacing between carbon planes  
 $\epsilon$  - interaction parameter  
 $\eta$  - reduced density  
 $\rho$  - density  
 $\phi$  - fugacity coefficient  
 $\sigma$  - molecular diameter  
 $\Gamma^{\text{ex}}$  - excess  
 $\Psi$  - fluid-solid potential

### *Superscripts*

attr - attractive term  
LCL - local property  
rep - repulsive term

### *Subscripts*

A - component A in binary mixture  
B - component B in binary mixture  
atoms - refers to atom density  
bulk - property of bulk fluid  
calc - fugacity defined by the equation of state  
ff - fluid-fluid property  
fs - fluid-solid property

## **Chapter 1: INTRODUCTION AND BACKGROUND**

Adsorption is defined as the attraction of fluid particles onto the surface of a solid with the formation of an “adsorbed phase”. It is a useful separation process which often requires no addition of heat. This thesis looks at some experiments involving this problem, as well as the utilization of other separations techniques, in the area of food processing. The significance of this work lies in the fact that natural cherry flavoring (benzaldehyde) is much more valuable than artificial flavoring. Even though the natural and artificial flavors are identical in taste, “natural flavoring” labeling is important to the food industry. Furthermore, cherry pits are an immense waste product which cherry companies must deal with. If a process could be developed to recover some of the remaining flavor from the cherry pits, it might prove economically beneficial to such companies. There is also an environmental issue with cherry pits in cyanide release. The thesis work of Cassandra Smith has suggested that air stripping may be the solution to making any liquid waste products from this process meet the environmental regulations.

Adsorption modeling is also dealt with in this thesis. Unlike in the case of cherry flavoring which involves liquid systems, the models presented here will be for gas systems interacting with activated carbon. Some of the primary gases of interest are methane, ethane, propane, ethylene, propylene, carbon dioxide, toluene, and nitrogen. The ESD equation of state will be combined with the Simplified Local Density model first developed in the dissertation of Bharath Rangarajan. The SLD model was first used with the van der Waals (Rangarajan, 1992) and Peng-Robinson (Subramanian, 1995) equations. While these equations did give some promising results, the ESD equation of

state does better in many cases of pure component adsorption (e.g. methane, ethylene). Furthermore, it does a much better job in calculating mixture adsorption than does the Peng-Robinson equation as will be seen with various fits of ethane-methane and ethylene-methane. However, a fit to toluene-carbon dioxide adsorption data shows that the ESD still only gives qualitative predictions in some cases. Currently, the mixture model assumes uniform particle size, which is an unrealistic assumption for some cases.

Despite some its weaknesses, the ESD equation of state still serves as a good predictor of bulk fluid conditions. It also gives excellent engineering estimates for adsorption in many systems. Eventually, it is hoped that this equation will be adopted for use in process simulators and other software, both for bulk and adsorption calculations. Further work still needs to be done with the SLD model. First, it must be modified to deal with the different particle sizes present in mixtures. Secondly, it must be modified to handle mixtures with more than two components. Once code is developed for these applications, then it might more easily be adopted for commercial use.

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## **Chapter 2: RECOVERY OF BENZALDEHYDE AND BENZYL ALCOHOL FROM CHERRY PITS**

### **INTRODUCTION**

A Phase I USDA grant was provided for developing a process to recover natural flavoring (benzaldehyde and benzyl alcohol) from cherry pits. This work was performed in conjunction with Natura, Inc (Lansing, MI). It is motivated by the fact that market prices for natural flavors are much higher than for artificial flavors. While being identical in taste quality, artificial and natural flavor components can be distinguished by their deuterium distributions (Hagedorn, 1992).

This work required several experimental steps of process development. It was necessary to develop a hydrolysis procedure which would provide the greatest concentration and quantity of benzaldehyde while minimizing its oxidation to benzoic acid. Filtration was also required in order to eliminate plugging in the bed and tubing. Adsorption, the heart of the process, involved a large amount of experimental work aimed toward optimizing several variables. Success was measured by the characteristic breakthrough curves. Finally, several efforts have given limited success in the regeneration and purification of the aromatics.

### **HYDROLYSIS**

Based on past experimental work on this project, the same hydrolysis conditions were agreed upon throughout all of the adsorption runs performed. The pits were ground up and then added to water preheated to 50°C. For each solution, a 5:1 water-to-pit mass

ratio was used. A discussion of this choice will be given later on. The water and pits were mixed together for 1 hour and then put through the filtration process described in the next section.

Due to differences in the pit yields from previous work, various tests were performed analyzing optimal hydrolysis conditions as well as the chemical processes occurring during hydrolysis. Tests were done with water-to-pit ratios, amygdalin conversion, mandelonitrile conversion, kernel and shell contributions, and pre-heating of the pits.

Based on information from two different papers (Li et al., 1992; Zheng and Poulton, 1995), the pits are expected to contain quantities of amygdalin and mandelonitrile. These compounds are known to break down in water producing both cyanide and benzaldehyde. A 0.5 gram quantity of amygdalin (molecular mass: 457.42) was added to 400 mL of hydrolyzate at 50°C and found to mostly break down into benzaldehyde (molecular mass: 106.12) after about 15 minutes of mixing. Table 2-1 gives the gas chromatography data of this experiment. It shows the hydrolyzate before and after the amygdalin addition. The lower and higher retention times correspond to benzaldehyde and benzyl alcohol (molecular mass: 108.1) respectively. The data shows a net gain of  $9.64\text{E-}4$  moles of benzaldehyde. Since  $10.93\text{E-}4$  moles of amygdalin were added, this experiment shows that 0.88 moles of benzaldehyde were created per mole of amygdalin added. One mole of amygdalin stoichiometrically breaks down into one mole of benzaldehyde when completely hydrolyzed. This experiment is not far from confirming this result. Note the 10% reported drop in benzyl alcohol concentration during this addition. This is likely to be due to the normal variations seen on this piece of

equipment. Apparently, amygdalin plays little or no direct role in the presence of benzyl alcohol.

Table 2-1: Results of Amygdalin Breakdown in Hydrolyzate

<u>GC Retention Time (min.)</u>	<u>Peak Area</u>	<u>Parts Per Million</u>	<u>Moles (<math>10^{-5}</math>)</u>
Hydrolyzate			
2.76 (benzaldehyde)	0.4592	25.4	9.57
4.22 (benzyl alcohol)	0.9324	51.5	19.06
Hydrolyzate + Amygdalin			
2.72 (benzaldehyde)	5.0862	281.0	105.92
4.20 (benzyl alcohol)	0.8345	46.1	17.06

A similar test with similar results was also done for mandelonitrile (molecular mass: 133.15). Mandelonitrile was more difficult to quantitatively measure due to its tendency to stick to the sides of glassware; thus, a larger margin of error should be allowed for this experiment. Approximately 0.5 mL of mandelonitrile was added to 300 mL of hydrolyzate. The results are shown in Table 2-2. The specific gravity of mandelonitrile is 0.95 grams per milliliter. Thus, a total of  $356.7E-5$  moles were added to the hydrolyzate. The experiment shows a corresponding  $297E-5$  mole increase in benzaldehyde. This means that 0.83 moles of benzaldehyde are formed per mole of mandelonitrile added to the hydrolyzate. Once again, the stoichiometric ratio should be 1:1 when completely hydrolyzed. Also, the observed benzyl alcohol concentration actually decreases by about 7% in this experiment—probably due to normal GC variations. As in the case of amygdalin, it is clear that mandelonitrile plays little or no direct role in the presence of benzyl alcohol.

**Table 2-2: Results of Mandelonitrile Breakdown in Hydrolyzate**

<u>GC Retention Time (min.)</u>	<u>Peak Area</u>	<u>Parts Per Million</u>	<u>Moles (<math>10^{-5}</math>)</u>
Hydrolyzate			
2.77 (benzaldehyde)	0.8310	45.9	12.98
4.23 (benzyl alcohol)	1.0317	57.0	15.82
Hydrolyzate + Mandelonitrile			
2.72 (benzaldehyde)	19.8320	1096	310
4.19 (benzyl alcohol)	0.9733	53.8	14.93

The pits were separated into their constituent kernels and shells in another test. The kernel accounts for about 80% of the total pit mass, and the shell makes up about 20%. Table 2-3 shows the results of this test on pits taken from the same bucket. First, a standard hydrolysis (5:1 water-to-pit mass ratio) was performed. A hydrolysis was then performed on a sample of kernels only at a 5:1 water-to-kernel ratio. Finally, a hydrolysis was performed on a sample of shells at a 5:1 water-to-shell ratio. The results show that a sample of kernels gives a 47% higher yield of benzaldehyde and a 117 % higher yield of benzyl alcohol than an equivalent mass of pits. On the other hand, a sample of shells gives 14% and 40% of the respective yields of benzaldehyde and benzyl alcohol in an equivalent mass of pits. Thus, the kernels make the larger contribution to the hydrolyzate concentrations of these chemicals. Note that the pits yield a 5:6 ratio of benzaldehyde to benzyl alcohol while the kernels yield a 1:2 ratio and the shells yield a 1:4 ratio. One would expect the hydrolysis with pits to yield concentration ratios somewhere between the kernel and shell hydrolyses. It seems that the presence of both shells and kernels might be facilitating some chemical interconversion between benzaldehyde and benzyl alcohol. More experiments should be done to confirm this hypothesis. The reasons for such an interconversion are unknown at this time.

**Table 2-3: Kernel and Shell Contributions to Hydrolyzate**

<u>Retention Time (min.)</u>	<u>Peak Area</u>	<u>Parts Per Million</u>
<b>Standard Hydrolysis</b>		
2.79 (benzaldehyde)	0.9030	49.9
4.26 (benzyl alcohol)	1.0900	60.2
<b>Kernel Hydrolysis</b>		
2.75 (benzaldehyde)	1.3247	73.2
4.22 (benzyl alcohol)	2.3679	130.8
<b>Shell Hydrolysis</b>		
2.79 (benzaldehyde)	0.1248	6.9
4.24 (benzyl alcohol)	0.4358	24.1

One other test involved pre-heating the pits to 30°C overnight in an attempt to curtail possible side effects from mold and residual fruit moisture on the surface of the shells. These results are shown in Table 2-4. While the benzaldehyde concentration increased slightly (within the normal range of data variation), the benzyl alcohol concentration went down by about 30%.

**Table 2-4: Effect of Pre-Warming Pits to 30°C before Hydrolysis**

<u>Retention Time (min.)</u>	<u>Peak Area</u>	<u>Parts Per Million</u>
<b>No Warming</b>		
2.80	0.6608	36.5
4.27	1.3391	74.0
<b>Warming</b>		
2.80	0.7404	40.9
4.26	0.9189	50.8

Another test involved adjusting water-to-pit mass ratios. These results are shown in Table 2-5. Ratios of 2:1, 3:1, 4:1, and 5:1 were compared for benzaldehyde and benzyl alcohol yield. 100 grams of pits were used in each experiment with the water quantity being adjusted to each of the ratios. The 5:1 ratio has the largest benzaldehyde yield,

while the 3:1 ratio has the largest benzyl alcohol yield. The 2:1 ratio shows a large drop-off in the concentration of each component as compared to the 3:1 ratio. It is suspected that the large quantity of solids in the 2:1 ratio begin to cause mass transfer limitations since most of the water absorbs into the ground pits. Due to the higher benzaldehyde yield, the 5:1 ratio has been chosen for the majority of the work.

**Table 2-5: Comparison of Water-to-Pit Mass Ratios in Hydrolysis**

<u>Retention Time (min.)</u>	<u>Peak Area</u>	<u>Parts Per Million</u>	<u>Yield (g)</u>
<u>5:1</u>			
2.77	0.8310	45.9	0.0230
4.23	1.0317	57.0	0.0285
<u>4:1</u>			
2.75	0.7160	39.6	0.0158
4.20	1.2307	68.0	0.0272
<u>3:1</u>			
2.67	0.6745	37.3	0.0112
4.20	2.0465	113.1	0.0339
<u>2:1</u>			
2.74	0.2436	13.5	0.0027
4.20	1.2416	68.6	0.0137

Based upon the above results, it is natural to consult the literature for further guidance regarding the origin and interconversion of benzaldehyde and benzyl alcohol. Reilly and coworkers (1986) discuss amygdalin conversion in peaches. Amygdalin first breaks down into prunasin which in turn breaks down into mandelonitrile. In a paper by Swain and Poulton (1994), black cherry seeds contain larger quantities of amygdalin in earlier stages of development than in later stages of development. Conversely, higher amounts of prunasin are found in the later stages of seed development. Also, the paper identifies enzymes associated with the stages of amygdalin breakdown. Amygdalin hydrolase catalyzes the breakdown of amygdalin to prunasin while GT-II (UDPG:prunasin glucosyltransferase) catalyzes the reverse reaction. Prunasin hydrolase

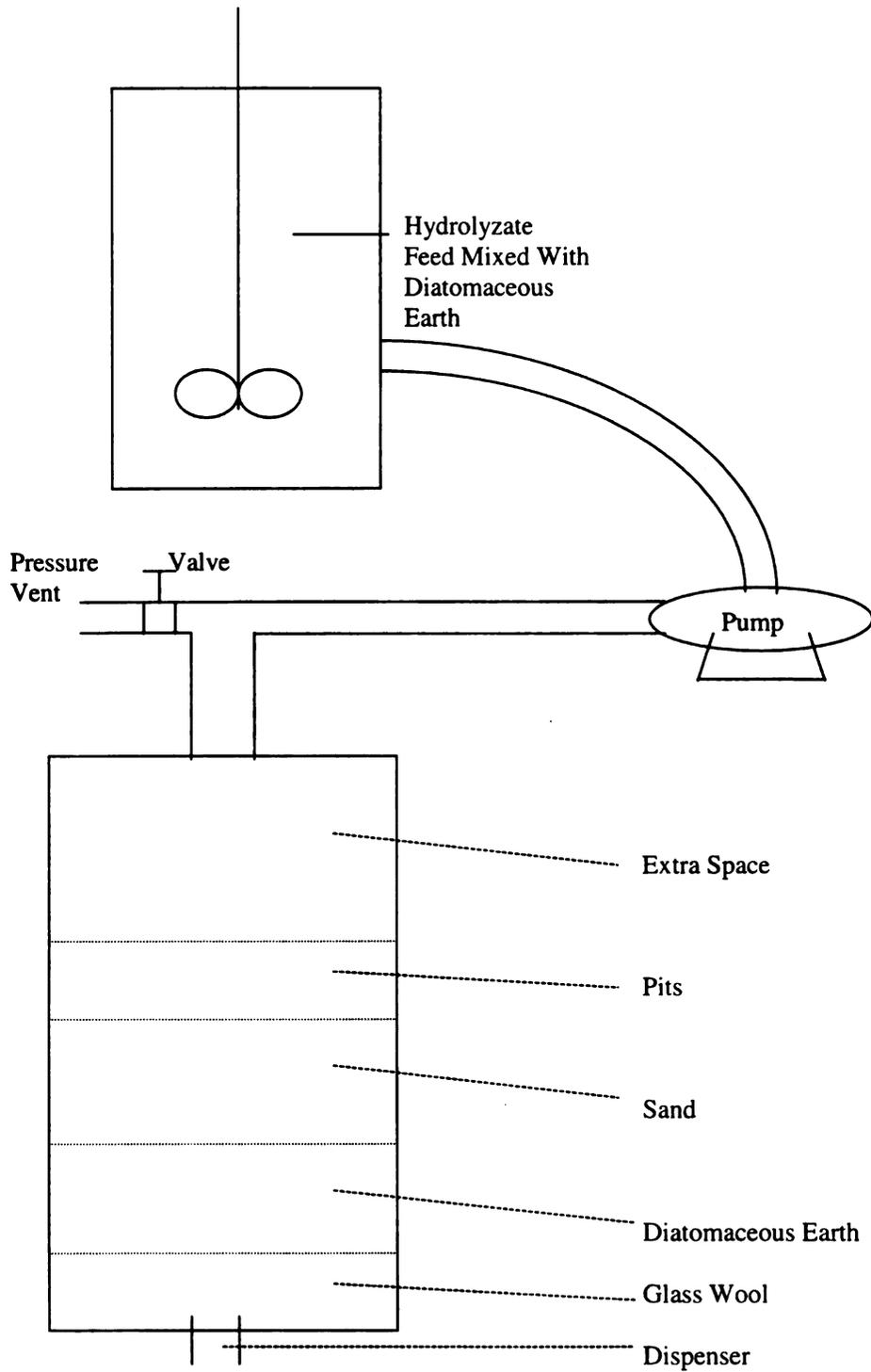
catalyzes the breakdown of prunasin to mandelonitrile while GT-I (UDPG:mandelonitrile glucosyltransferase) catalyzes the reverse reaction. Mandelonitrile lyase catalyzes the conversion of mandelonitrile into benzaldehyde and cyanide. Kawabe and Morita (1994) describe the role that a particular breed of fungus plays in interconverting benzaldehyde and benzyl alcohol. The paper also describes a fungus-facilitated mechanism for benzaldehyde and benzyl alcohol formation by identifying such precursors as L-phenylalanine, t-cinnamic acid, and 3-phenylpyruvic acid. A paper by Lamer and coworkers (1996) identifies another fungus responsible for benzaldehyde and benzyl alcohol interconversion and formulates another mechanism for their production. It lists styrene, 1-phenyl ethanone, and phenylacetaldehyde as other precursors.

## FILTRATION

The hydrolysis procedure yields a solution containing a wide variety of particle sizes. This made efficient filtration a challenging task—especially for large quantities of hydrolyzate. A couple of stages were necessary in removing particulates.

The first stage involved removing the cherry pit shells and kernels through a screen with a sieve size of 180 microns. This process was very quick, and it effectively removed all of the large particles. The hydrolyzate was poured into a pan with the screen built onto the bottom. The pits were emptied out of the pan as necessary.

The second stage was more complicated. It was performed in a metal cylinder with a diameter of about 3 inches and a length of about 15 inches. The following items composed the filter (bottom to top): 4 grams of glass wool, 32 grams of diatomaceous earth (normally used in swimming pool filters), 130 grams of sand, and 50 grams of cherry pits for the purpose of spreading liquid flow over the entire diameter of the filter. Figure 2-1 shows a schematic of this filter. A pump pushed the hydrolyzate through the filter from a feed tank. While this filter effectively removed all noticeable particulates from the hydrolyzate, the filter cake caused it to plug very quickly. The solution to this problem involved mixing diatomaceous earth into the hydrolyzate feed. It was found that maintaining 10 grams of diatomaceous earth per liter of hydrolyzate worked quite well throughout the duration of the filtration. While the diatomaceous earth increased the volumetric buildup of the filter cake, it made the filter cake sufficiently porous so that plugging was not as great of an issue.



**Figure 2-1: Filtration Schematic**

## ADSORPTION/BREAKTHROUGH

Figure 2-2 shows the apparatus used for conducting adsorption runs. The feed resided in a 20-L glass jar which in turn was placed in an ice bath. The chilled condition served to slow down bacterial growth in the hydrolyzate. PharMed tubing carried fluid from the bottom of the jar to the Masterflex pump. The tubing then ran from the pump to the top of the adsorption bed. The adsorption bed itself consists of a glass tube measuring 3 centimeters in diameter. Silicon stoppers were placed on the top and bottom openings in order to hold the contents. Glass wool was placed underneath the adsorbent in order to prevent spillage into the tubing. A clamped tube was placed at the top of the column in order to relieve the system of air when necessary. The beds ran completely filled with hydrolyzate. A three-way valve was placed at the bottom of the column for the purpose of convenient sampling.

These sets of experiments were aimed toward determining the optimal operating conditions for the adsorption of benzaldehyde and benzyl alcohol. The primary variables were the resin (adsorbent) bed size and the flow rate. Screening procedures in previous work have identified XAD-4 (from Rohm and Haas) and SP-850 (from Mitsubishi Chemical), as the best known resins for benzaldehyde adsorption. All of the adsorption runs performed with new resin at a flow rate less than or equal to 15 bed volumes per hour (Figures 2-3 through 2-5) show the breakthrough of benzaldehyde to be slow and linear. Benzaldehyde reaches 20% breakthrough in a 60 mL bed of XAD-4 after the elution of about 100 bed volumes of hydrolyzate at 15 bed volumes per hour (Figure 2-5). A similar bed of SP-850 at the same flow rate reaches 20% breakthrough at an elution of 200 bed volumes (Figure 2-4). Thus, SP-850 seems to have a higher capacity for

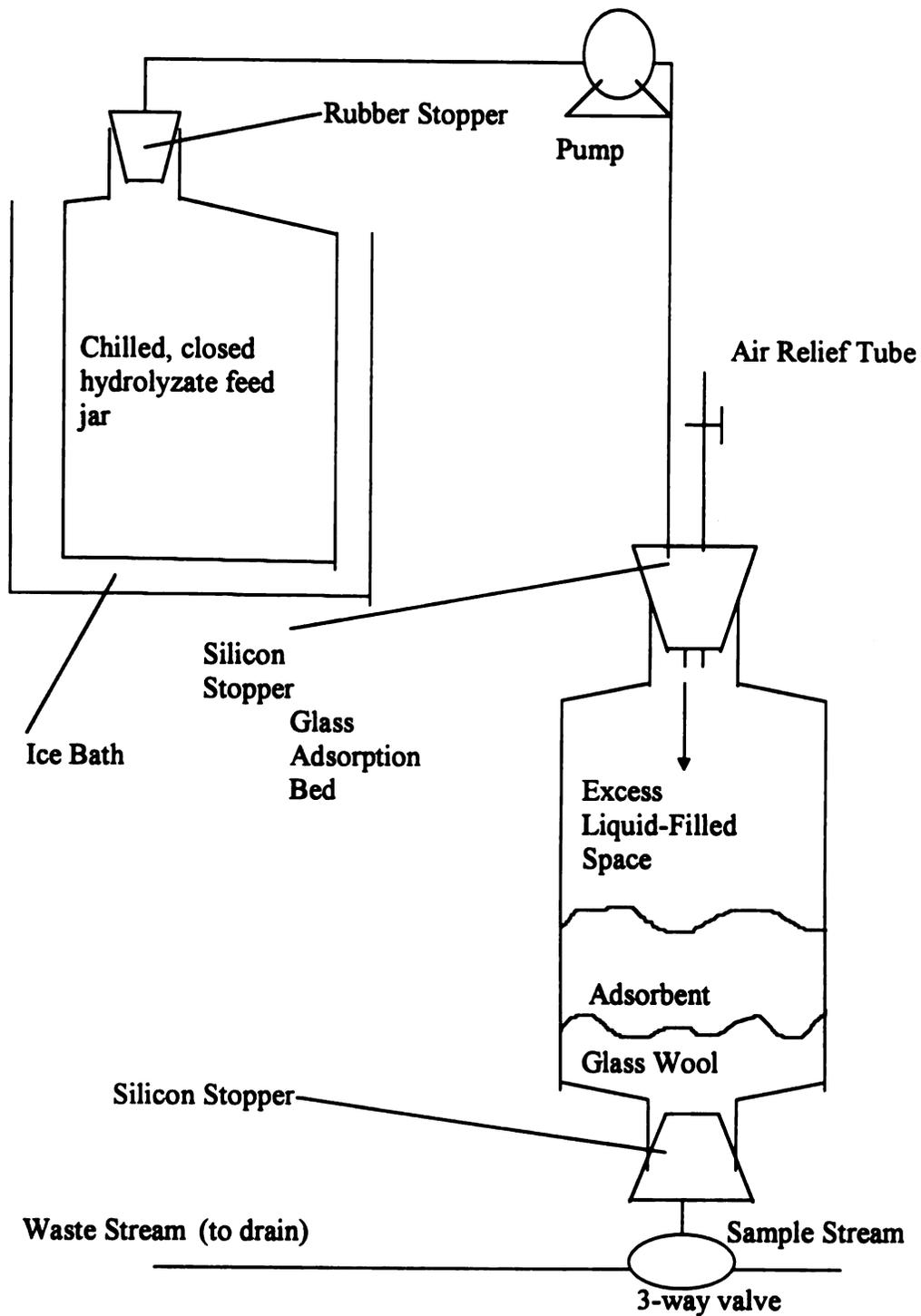
benzaldehyde. Note that a bed of 100 mL XAD-4 with a flow rate of 9 bed volumes per hour reaches 20% breakthrough at an elution of 300 bed volumes of hydrolyzate (Figure 2-3). This implies that the slower flow rate relative to the bed volume gives better adsorption performance. For these same runs, benzyl alcohol seems to reach its maximum at or above 100% breakthrough despite the more significant scatter.

Figures 2-6 and 2-7 show runs where the resins were reused. They had already been put through one cycle of adsorption and desorption before undergoing the runs shown. The regeneration was done with liquid carbon dioxide pressurized to about 1300 psig in the bed. In each case, about a 500-liter equivalent of carbon dioxide at room temperature and pressure was passed through the bed in order to remove any adsorbates. This work will be discussed further in the next section. The reused resin actually seems to show better performance. Figure 2-6 shows a 20% breakthrough for SP-850 at 600 bed volumes of effluent. Figure 2-7 shows a bed of XAD-4 similar to that in Figure 2-5. The bed of reused resin once again performs better—20% breakthrough at over 300 bed volumes of effluent as opposed to the 100 bed volumes of effluent shown in Figure 2-5. Furthermore, benzyl alcohol seems to take on a more linear breakthrough curve with the reused resin. In each case, the benzyl alcohol curve extends well beyond 200% breakthrough. This seems to imply that either the resin is not being completely regenerated before the second use or else benzyl alcohol is being formed by a chemical reaction. More investigation is needed in this matter.

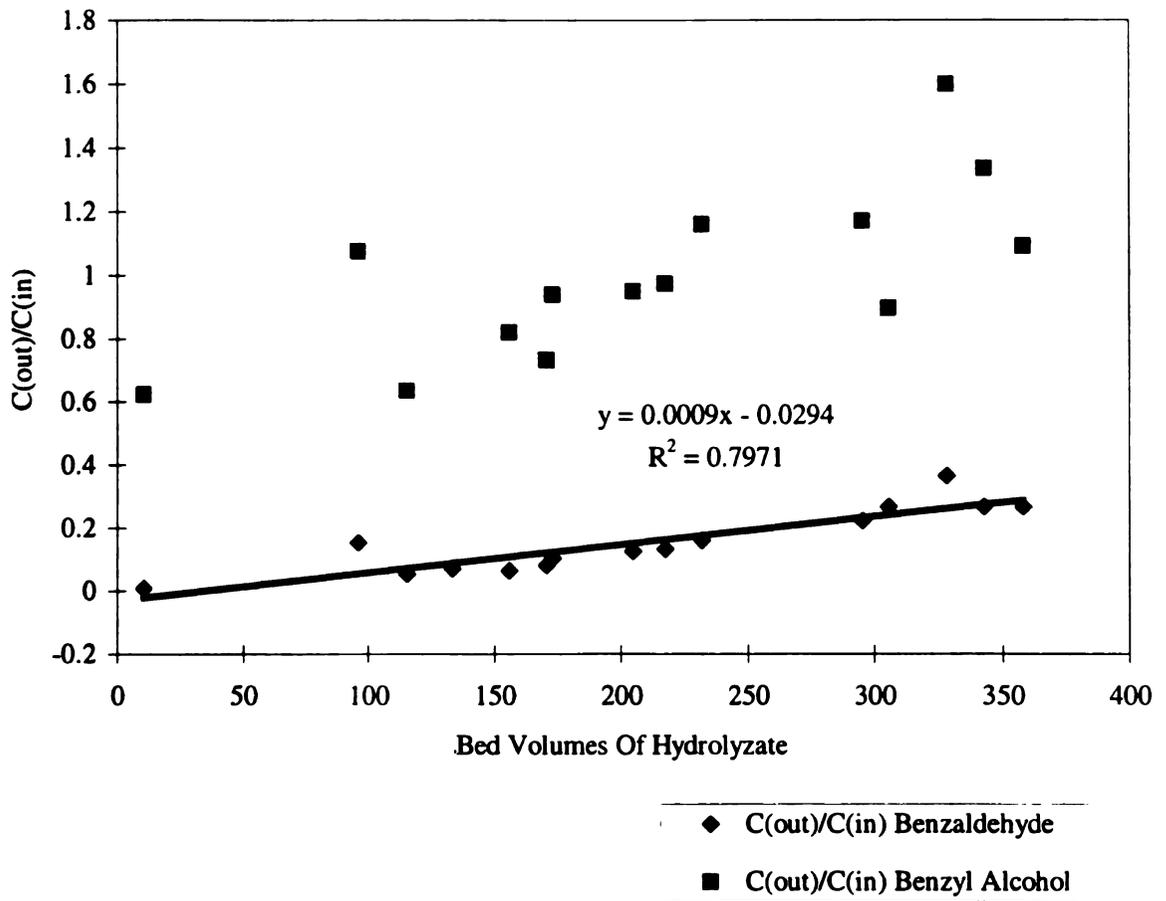
Figures 2-8 and 2-9 examine the effects of doubling the superficial velocity. In both cases, comparatively larger bed volumes and flow rates were tested. As in Figure 2-3, the flow rates are only 9 bed volumes per hour (30 mL/min). However, the superficial

velocities are doubled from 2.12 cm/min to 4.24 cm/min. The XAD-4 bed in Figure 2-8 shows a performance similar to its counterpart in Figure 2-3—20% breakthrough at an elution of nearly 300 bed volumes of hydrolyzate. The SP-850 bed in Figure 2-9 shows a similar performance despite some irregularities in benzaldehyde data early in the run. It exhibits 20% breakthrough at about 300 bed volumes of hydrolyzate elution. Thus, in this range of flows, superficial velocity does not appear to have a large effect on benzaldehyde adsorption. It is interesting to note that benzyl alcohol seems to exhibit a maxima in Figure 2-9.

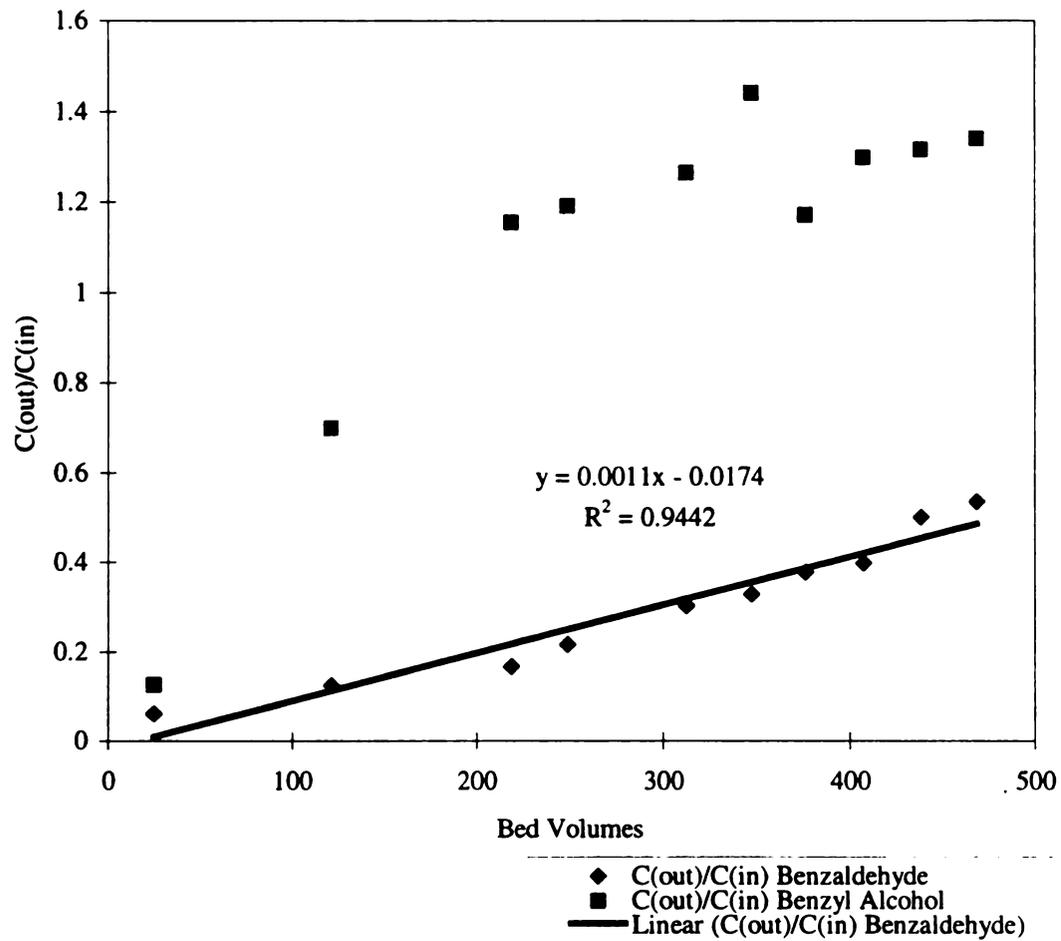
It is important to note that feed concentration is not kept perfectly constant throughout each of these runs. Figures 2-10 and 2-11 show typical fluctuations for an adsorption run. During each of these runs, the feed tank was being refilled every few hours. This accounts for the various spikes in the graphs. Note that the benzaldehyde and benzyl alcohol concentrations do not change greatly relative to one another. The benzaldehyde concentration hovers near 45 ppm in both Figures 2-10 and 2-11, while the benzyl alcohol concentration hovers near 15 ppm in each case. This may appear to conflict with some of the data presented in the Hydrolysis section, but the hydrolyzate concentrations do vary with different batches of pits.



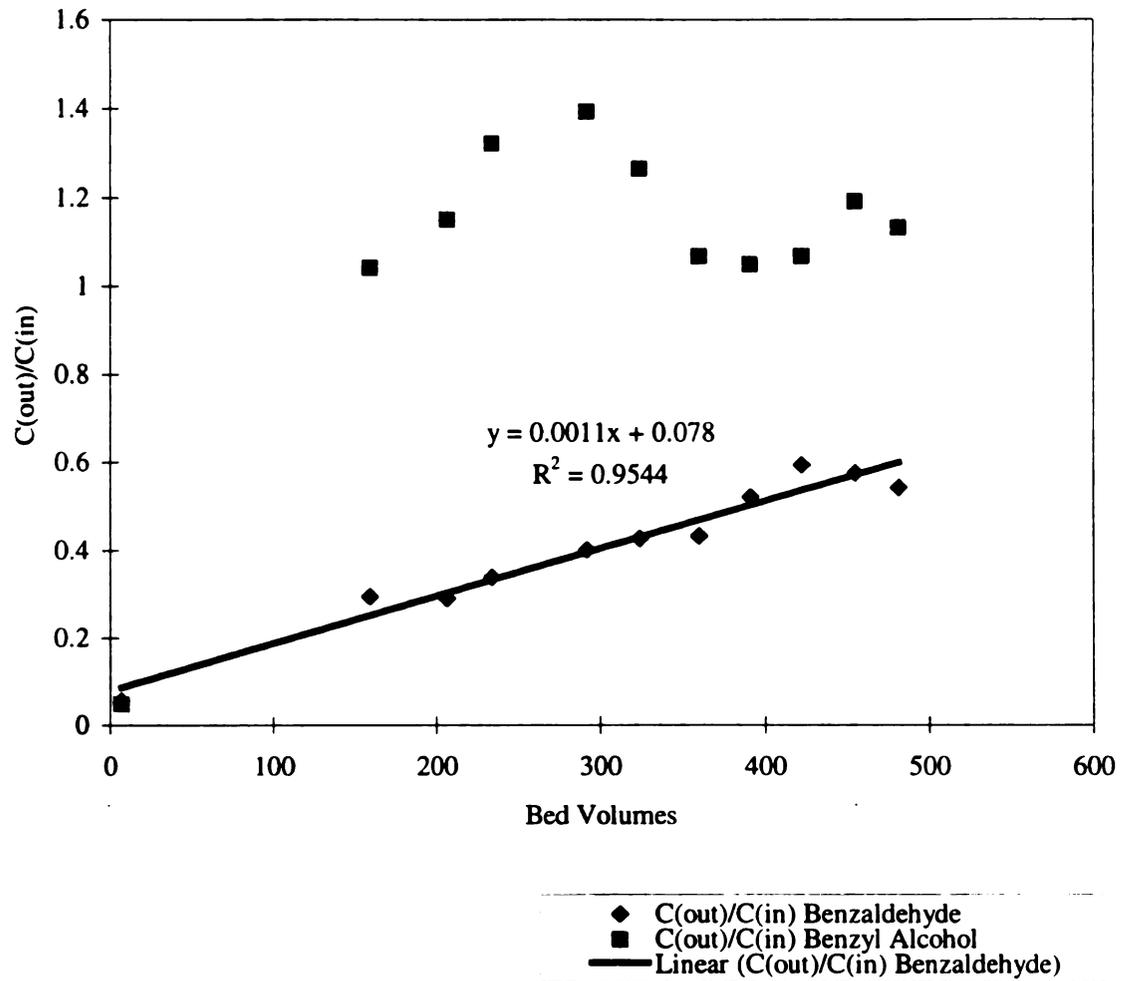
**Figure 2-2: Adsorption Apparatus**



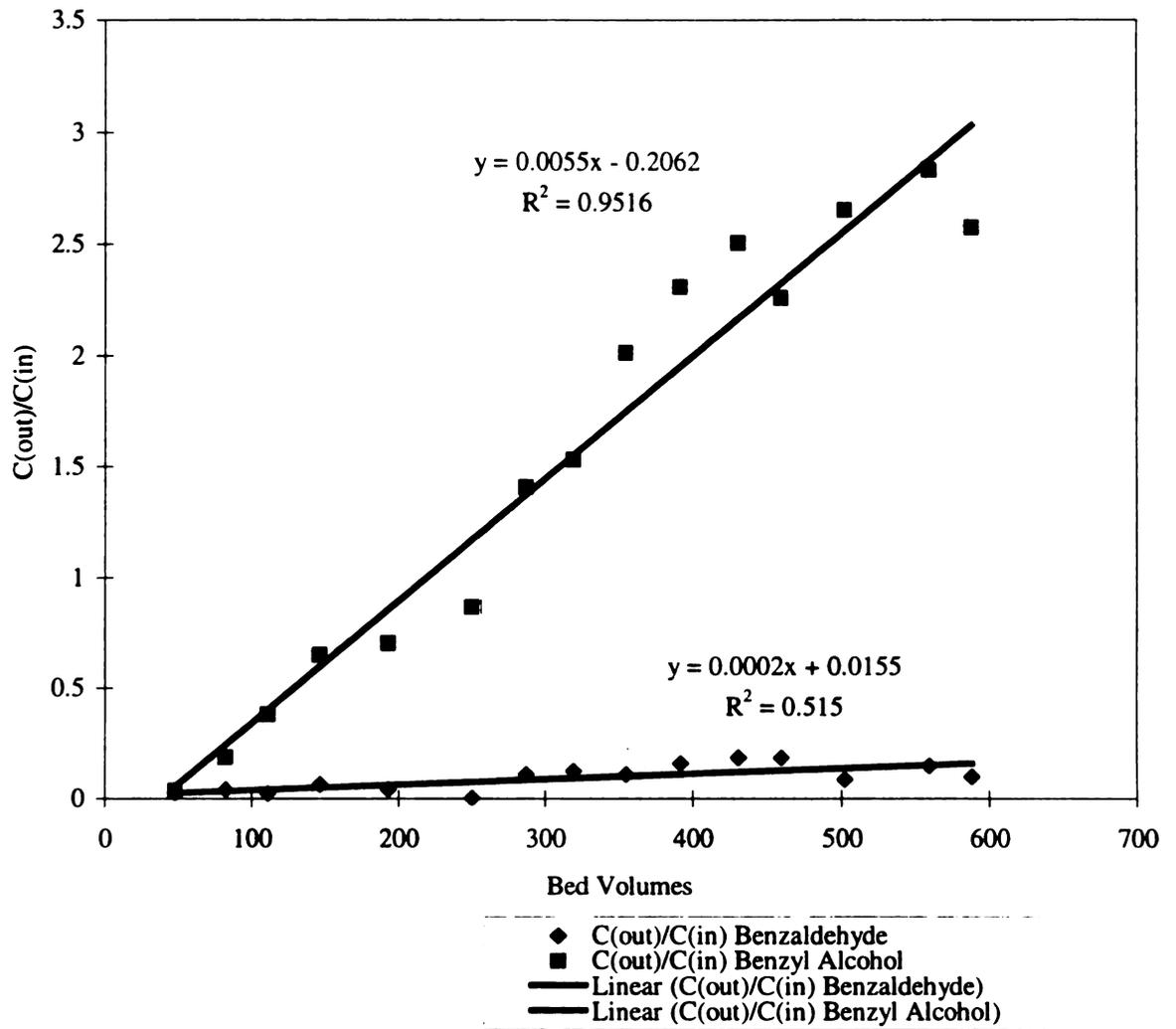
**Figure 2-3: Adsorption Test on 100 mL XAD-4 resin, 15 mL/min flowrate (9 bed volumes per hour, superficial velocity: 2.12 cm/min).**



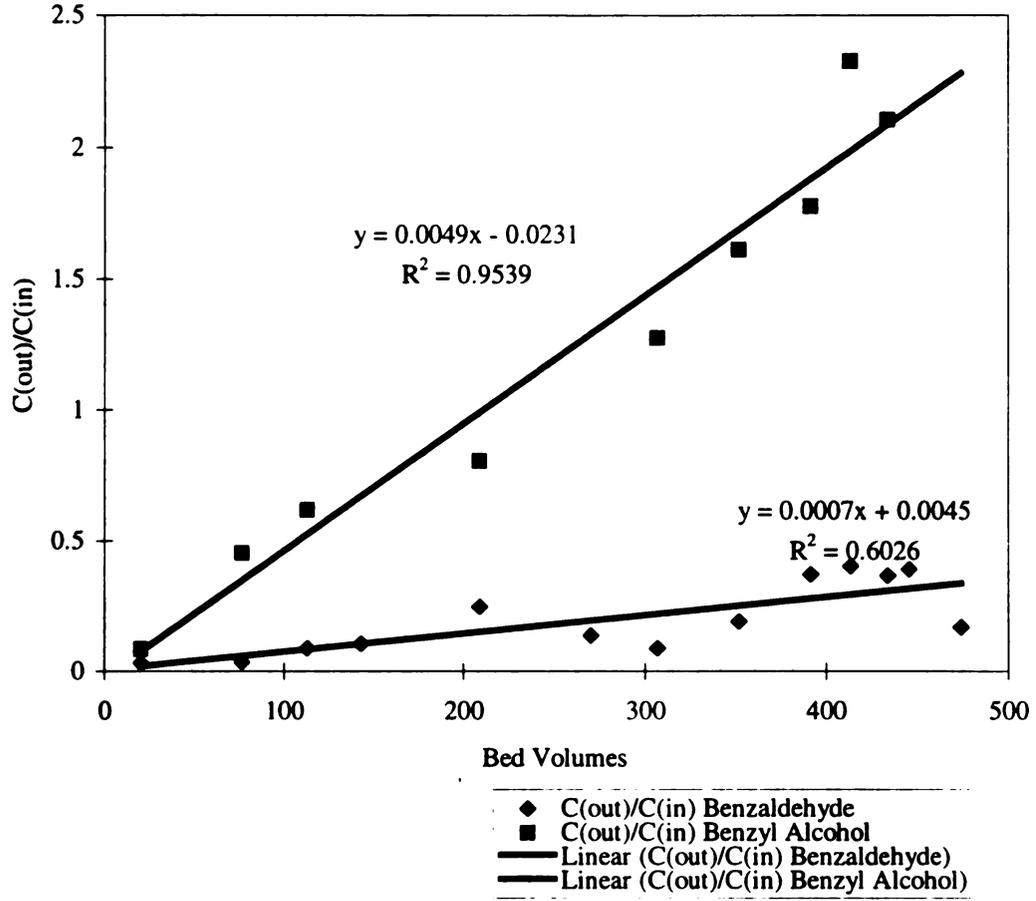
**Figure 2-4: Adsorption test on 60 mL SP-850 at 15 mL/min hydrolyzate flow (15 bed volumes per hour, superficial velocity: 2.12 cm/min).**



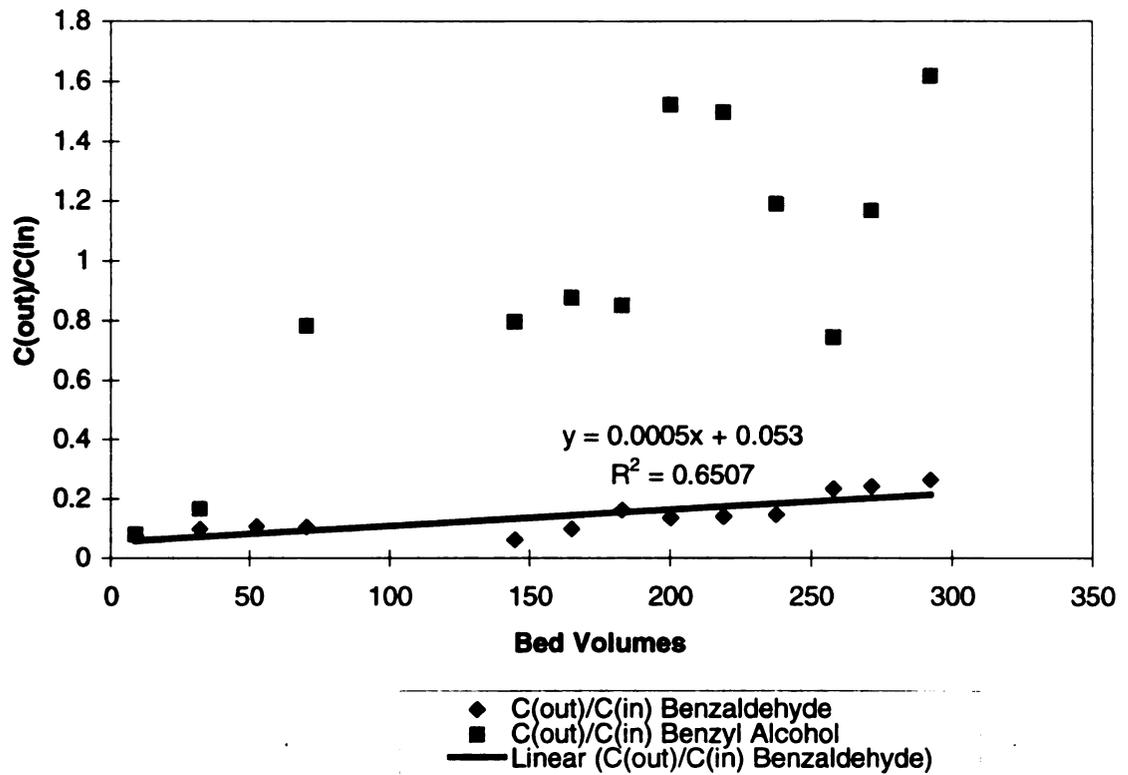
**Figure 2-5: Adsorption test on 60 mL XAD-4 with flow at 15 mL/min (15 bed volumes per hour, superficial velocity: 2.12 cm/min).**



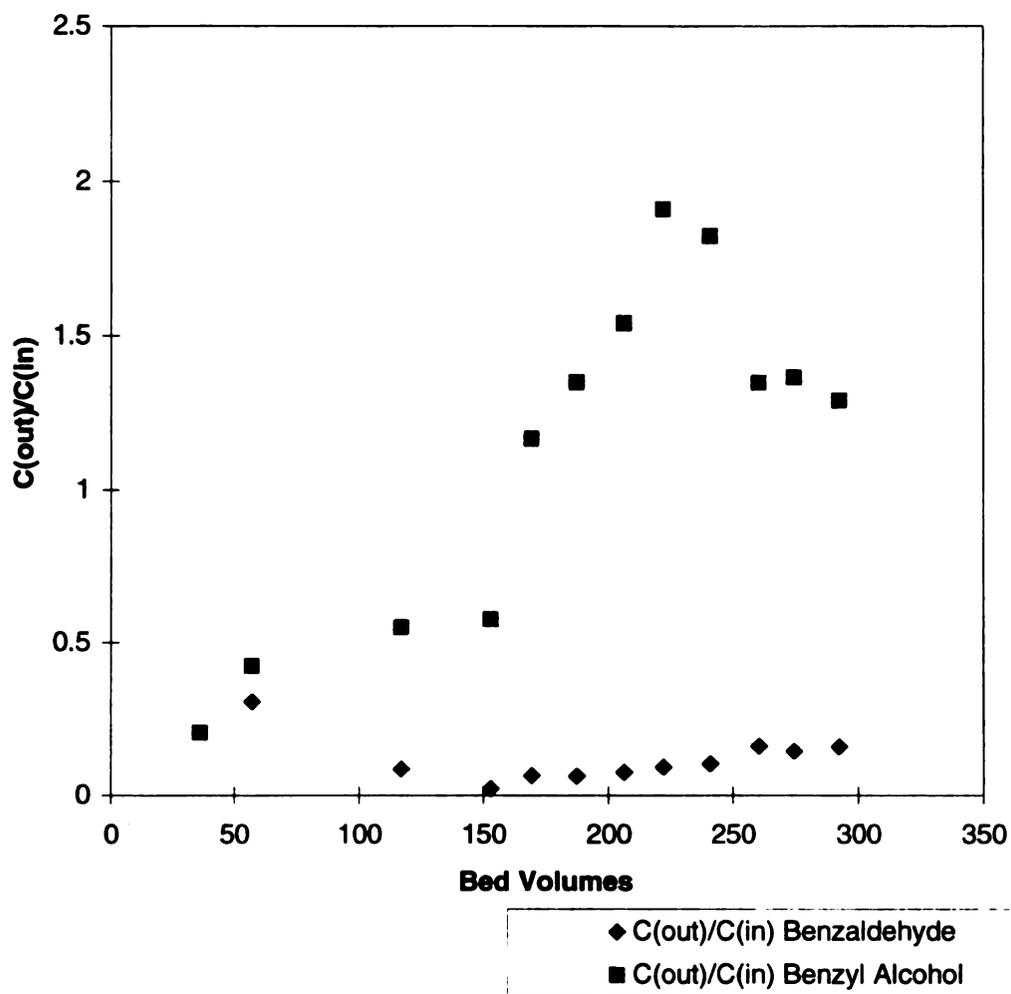
**Figure 2-6: Adsorption test on 60 mL of SP-850 reused once with a flow rate of 15 mL/min (15 bed volumes per hour, superficial velocity: 2.12 cm/min).**



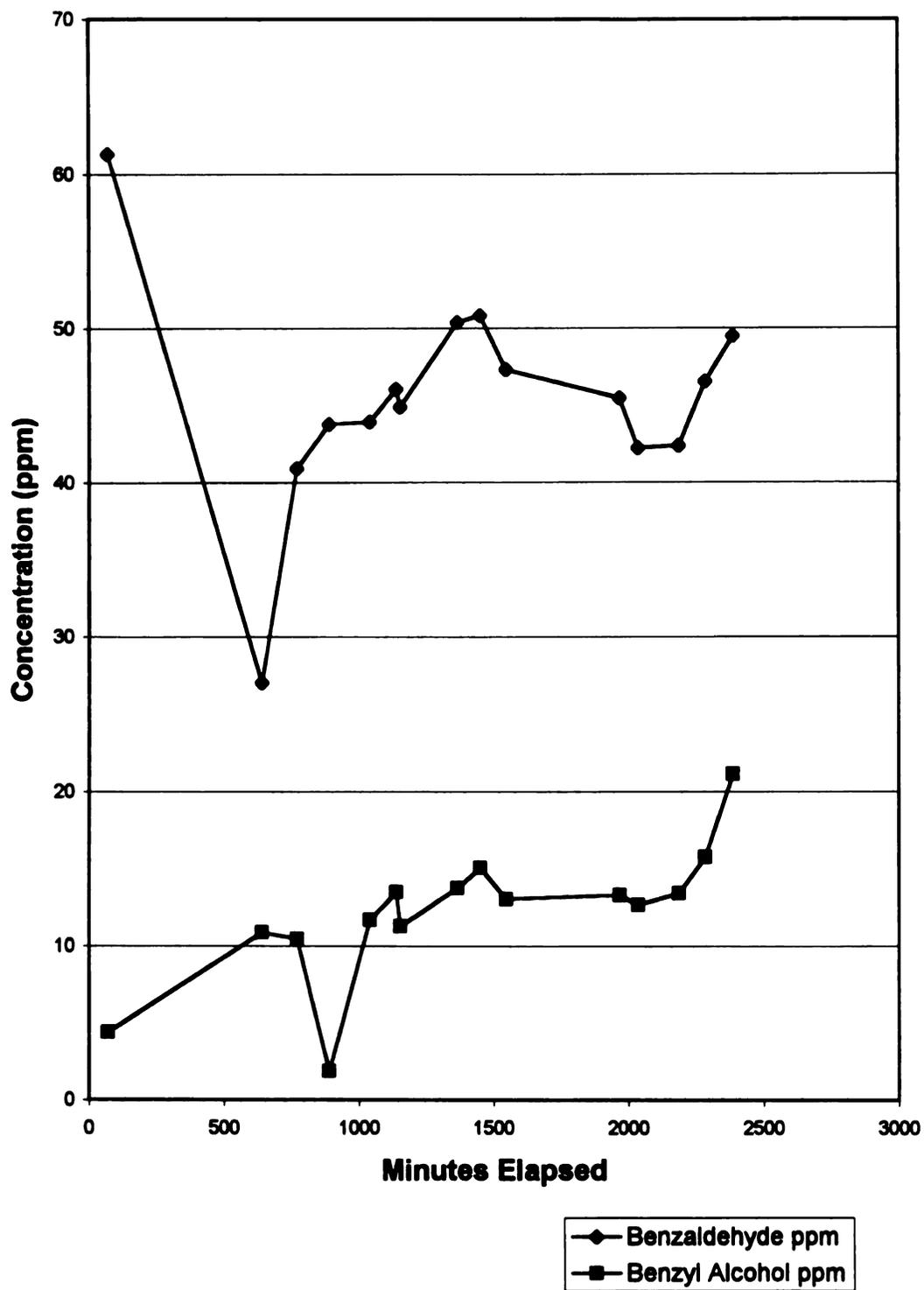
**Figure 2-7: Adsorption testing on 55 mL of reused XAD-4 with a flow rate of 15 mL/min (16.4 bed volumes per hour, superficial velocity: 2.12 cm/min).**



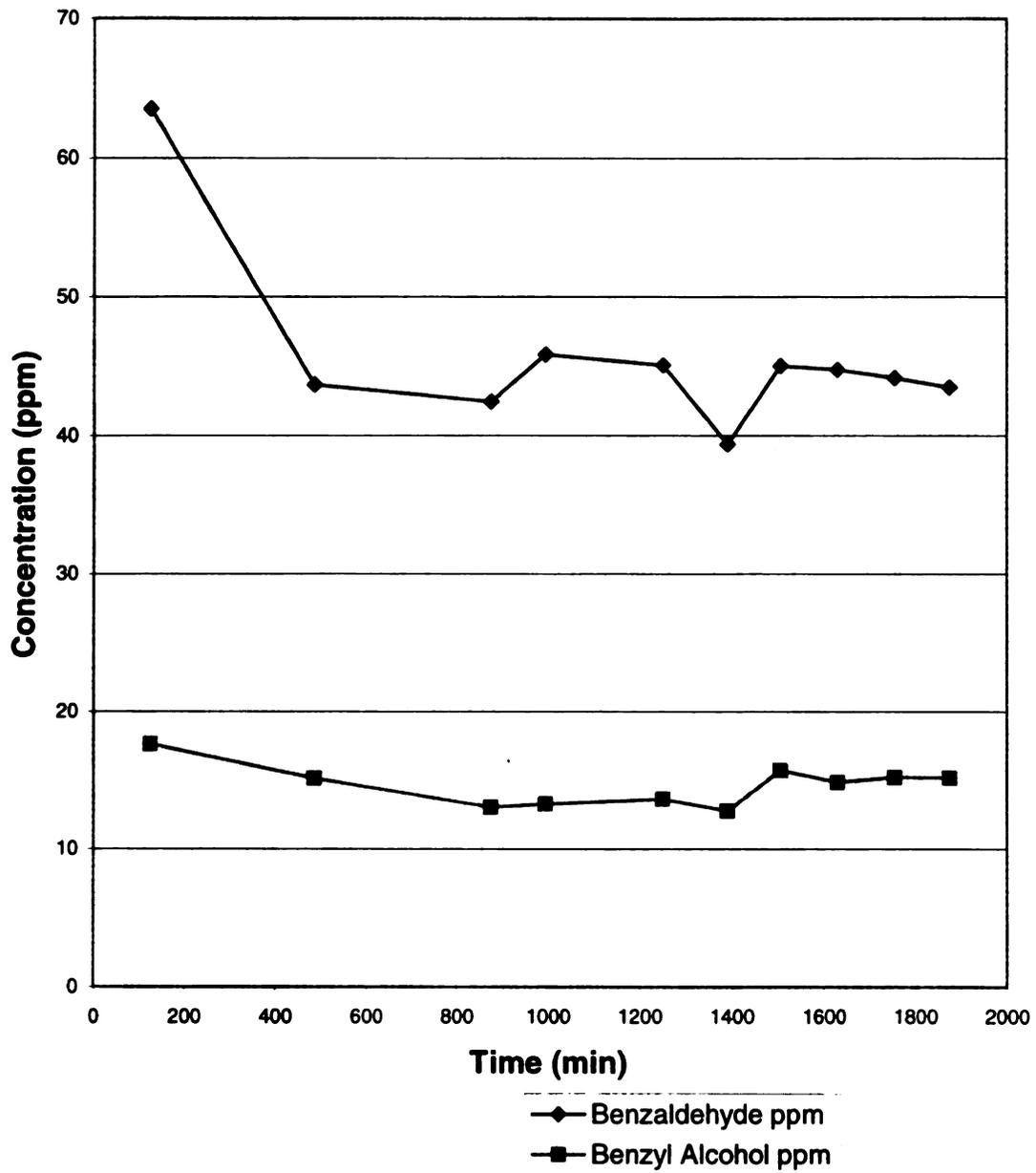
**Figure 2-8: Adsorption test on 200 mL XAD-4 with a flow rate of 30 mL/min (9 bed volumes per hour, superficial velocity: 4.24 cm/min).**



**Figure 2-9: Adsorption test on 200 mL SP-850 with a flow rate of 30 mL/min (9 bed volumes per hour, superficial velocity: 4.24 cm/min).**



**Figure 2-10: Benzaldehyde and Benzyl Alcohol Inlet Concentrations as Functions of Time Corresponding to the Run in Figure 2-3**



**Figure 2-11: Benzaldehyde and Benzyl Alcohol Inlet Concentrations as Functions of Time Corresponding to the Run in Figure 2-4**

## REGENERATION

After adsorption, the resin is regenerated with carbon dioxide pressurized to 1300 psig in order to obtain the desired components. While carbon dioxide doesn't have the best solubility properties, it is a relatively inexpensive gas. Furthermore, its liquid and gaseous properties can both be utilized at room temperature without any heating—only pressurization and depressurization. In its pressurized state, the liquid carbon dioxide passes through the bed and removes adsorbates from the pores of the resin. It is then depressurized into its gaseous state where it relinquishes its solutes. This is where the product is collected in this stage. Care must be taken to prevent the lines from freezing during depressurization. The resulting product is an aqueous solution many times more concentrated with the desired components than the hydrolyzate. The product contains water because of the moisture remaining in the bed after adsorption. Also, this product is a brown color. Gas chromatography reveals the presence of various unknowns as shown in Tables 2-6 and 2-7. Benzaldehyde is at 2.94 minutes on Table 2-6 and 2.92 minutes on Table 2-7. Benzyl alcohol is at 4.41 minutes on Table 2-6 and 4.40 minutes on Table 2-7.

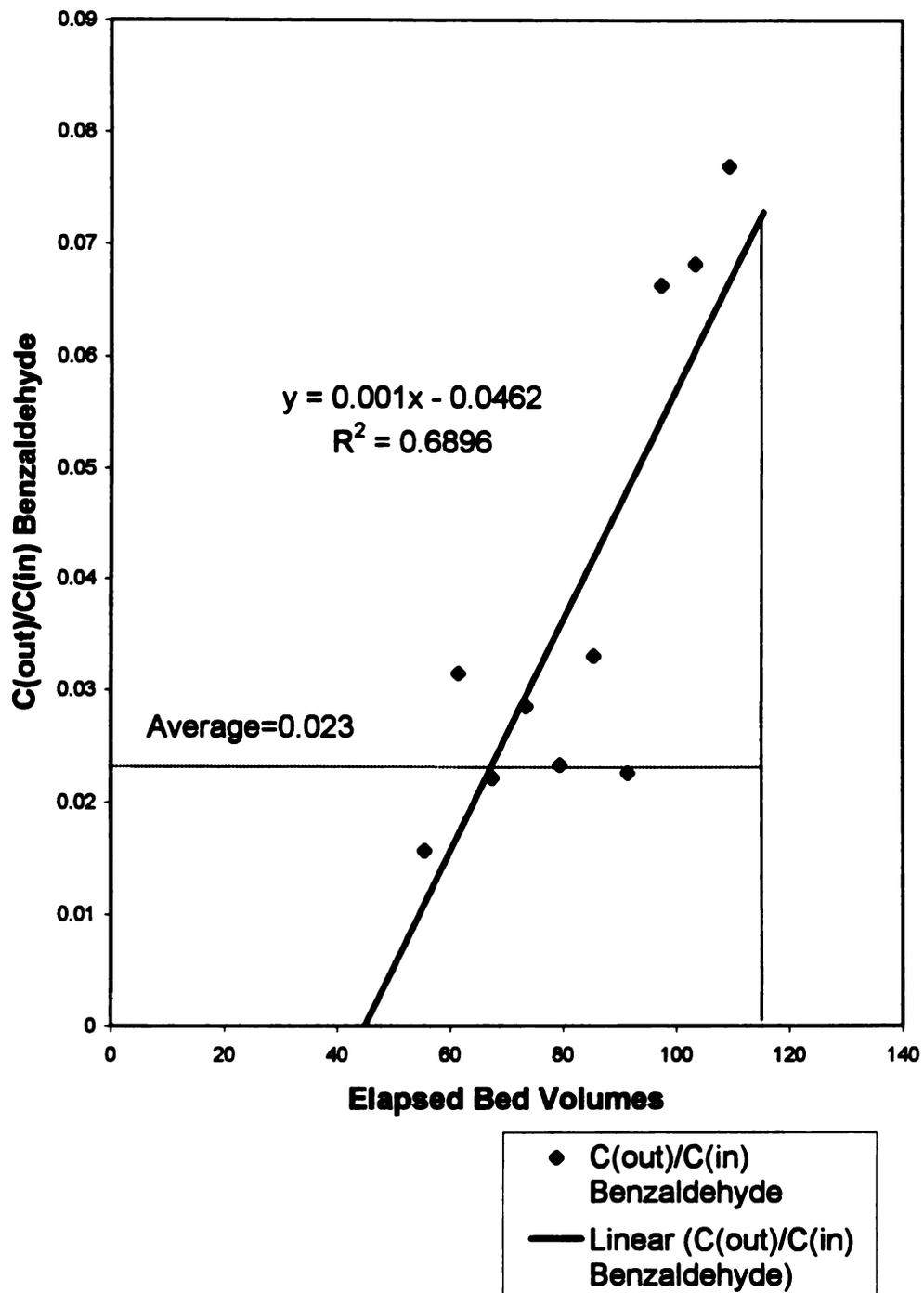
Table 2-6: GC Analysis of a Sample Regenerated from XAD-4

<u>Retention Time (min)</u>	<u>Peak Area</u>	<u>Parts Per Million</u>
2.94 (benzaldehyde)	124.91	6901
4.41 (benzyl alcohol)	51.63	2852
5.38	3.33	
7.10	8.16	
13.79	2.29	

**Table 2-7: GC Analysis of a Sample Regenerated from SP-850**

Retention Time (min)	Peak Area	Parts Per Million
0.18	2.31	
0.20	3.92	
2.92 (benzaldehyde)	112.38	6209
4.40 (benzyl alcohol)	40.09	2215
5.37	3.95	
7.06	4.70	
8.42	1.49	
11.43	1.06	
13.69	1.59	

The focus will now be shifted toward analyzing the efficiency of the regeneration step. Figure 2-12 shows the benzaldehyde breakthrough curve for the sample under consideration. This curve is needed for calculating the total amount of benzaldehyde adsorbed onto the resin. A linear regression will represent the portion of the data breaking through. The first step is to find the area under the breakthrough curve over the entire flow range of the run. The second step is to calculate the average  $C(\text{out})/C(\text{in})$  ratio over the entire range of the run, which turns out to be 0.023. This means that, on average, 97.7% of the inlet benzaldehyde concentration is adsorbed over the course of the entire run. For this experiment, the inlet benzaldehyde concentration averaged about 44 ppm over the 120 bed volumes fed (12 liters). Thus, 43 ppm of that amount was adsorbed throughout the run on average. This gives a total of 0.52 grams of benzaldehyde adsorbed.



**Figure 2-12: Adsorption Run on 100 mL XAD-4 Bed at 10 mL/min hydrolyzate flow.**

This sample was regenerated with the equivalent of 224 liters of carbon dioxide at room temperature and pressure at a flow rate between 2 and 3 liters per minute measured after depressurization. Three samples were taken as shown in Table 2-8A. Sample A was taken from the first 60 liters of carbon dioxide passed through the system. This is when most of the water is flushed out of the resin bed; hence, the comparatively large volume. Sample B was taken from the remaining 160 liters passed. This sample has a smaller volume but is much more concentrated. Sample C was taken from washing the sample chamber and tubing with ethanol. Judging by the significant concentration of the sample, this portion of the experiment cannot be ignored. The total benzaldehyde mass recovered from the three samples was 0.1712 grams. This means that 33% of the adsorbed benzaldehyde was recovered by regeneration.

**Table 2-8A: Regeneration Samples From the Run in Figure 2-12**

<b>Label</b>	<b>Volume (mL)</b>	<b>Benzaldehyde ppm</b>	<b>Benzaldehyde mass (g)</b>
<b>A</b>	28.5	658	0.0188
<b>B</b>	6.8	9111	0.0620
<b>C</b>	11	8221	0.0904

It is not certain whether the amount of carbon dioxide used maximizes the yield. Further work contributed by Greg Donath and Ryoko Yamasaki gives more information regarding possible inefficiencies in this stage. Table 2-8B gives a mass balance on benzaldehyde adsorption and regeneration from 55 mL of resin. Adsorption is represented with a positive number while desorption is represented with a negative number. The amount adsorbed was calculated in a manner similar to the previous system shown. After adsorption, the resin was rinsed and stored in water until the regeneration could be done. The benzaldehyde content of this water was analyzed. After the CO<sub>2</sub> regeneration was completed, the regeneration equipment was rinsed with propanol in

order to recover any residual desorbed material. The resin was then soaked in 100 mL propanol in an attempt to recover anything remaining on the resin. The data shows that only 40% of the benzaldehyde adsorbed on the resin can be accounted for by current methods.

**Table 2-8B: Benzaldehyde Mass Balance for CO<sub>2</sub> Regeneration**

<u>Step</u>	<u>Mass (g)</u>	<u>% of Adsorbed Mass</u>
Adsorption	2.69E-4	100
Water Wash/Storage	-3.20E-6	-1.2
CO <sub>2</sub> Regeneration	-7.97E-5	-29.6
System Propanol Wash	-2.08E-5	-7.7
Resin Wash with Propanol	-2.97E-6	-1.1
Mass Unaccounted For	1.62E-4	60.3

A similar balance was done for benzyl alcohol. The same experimental steps were analyzed and are shown in Table 2-8C. What is interesting about this experiment is that 20% more benzyl alcohol is reported as recovered than the amount originally adsorbed. This apparent phenomenon should be examined more deeply in future work.

**Table 2-8C: Benzyl Alcohol Mass Balance for CO<sub>2</sub> Regeneration**

<u>Step</u>	<u>Mass (g)</u>	<u>% of Adsorbed Mass</u>
Adsorption	5.66E-5	100
Water Wash/Storage	-2.29E-5	-40.5
CO <sub>2</sub> Regeneration	-3.19E-5	-56.4
System Propanol Wash	-6.09E-6	-10.8
Resin Wash with Propanol	-6.44E-6	-11.4
Mass Unaccounted For	-1.07E-5	-19.1

## PRODUCT PURIFICATION EXPERIMENTS

Different efforts have been made to further concentrate and isolate benzaldehyde and benzyl alcohol from the regenerated sample. The GC data shown in the previous section implies the presence of some heavier substances (Tables 2-6 and 2-7). The most logical first course of action would be to do an initial distillation, separating the lighter components from the heavier components. This experiment was tried with the 3 mL sample of regenerate shown in Table 2-9. This sample is not related to the regeneration data previously shown. Each component's peak area is quantitated as a percentage of the total area of all peaks recorded on the GC.

Table 2-9: GC Profile of Original Regenerate

Retention Time (min)	Peak Area	% Area of All Peaks	Parts Per Million
0.15	2.07	1.32	
0.17	4.80	3.06	
0.47	6.28	4.00	
0.54	1.93	1.23	
2.94 (benzaldehyde)	77.38	49.30	4275
4.42 (benzyl alcohol)	46.33	29.52	2560
5.40	2.35	1.50	
7.12	3.30	2.10	

The above sample was separated into three different fractions via a distillation column with a boiler and water-cooled condenser. Before distilling, argon was put through the system in order to remove the air. Oxygen has a tendency to oxidize benzaldehyde to benzoic acid. Table 2-10 shows the composition of Fraction A. This consists of the first 0.5 mL boiled and condensed. Note that this fraction is 61% more concentrated with benzaldehyde than the original. It is also 81% more concentrated with benzyl alcohol than the original sample.

**Table 2-10: Fraction A—The First 0.5 mL Boiled Over**

<b>Retention Time (min)</b>	<b>Peak Area</b>	<b>% Area of All Peaks</b>	<b>Parts Per Million</b>
0.17	4.53	1.75	
0.47	6.95	2.69	
0.54	9.16	3.55	
2.94 (benzaldehyde)	124.91	48.36	6901
4.42 (benzyl alcohol)	83.68	32.40	4623
7.11	13.72	5.31	

Table 2-11 shows a second 1 mL sample (Fraction B) boiled from the same feed pot. It contains 29% and 133% of the respective concentrations of benzaldehyde and benzyl alcohol in the original sample. Table 2-12 shows the composition of the remaining 1.5 mL in the feed pot (Fraction C). It contains 0.6% and 36.4% of the respective concentrations of benzaldehyde and benzyl alcohol in the original sample. Note the high concentration of the component at 7.1 minutes. While some of it is being carried over into the distillate products, it is still 16 times more concentrated in the remaining bottoms than in the original regenerate. This indicates that this product is being separated away from benzaldehyde and benzyl alcohol.

**Table 2-11: Fraction B—A Second Distilled Sample of 1 mL**

<b>Retention Time (min)</b>	<b>Peak Area</b>	<b>% Area of All Peaks</b>	<b>Parts Per Million</b>
0.17	1.61	1.62	
0.19	1.27	1.28	
2.93 (benzaldehyde)	22.76	23.00	1257
4.42 (benzyl alcohol)	61.77	62.42	3413
5.39	1.10	1.11	
7.13	1.20	1.21	

**Table 2-12: Fraction C—The Remaining 1.5 mL of Bottoms**

<u>Retention Time (min)</u>	<u>Peak Area</u>	<u>% Area of All Peaks</u>	<u>Parts Per Million</u>
0.17	3.19	6.02	
0.20	2.12	3.99	
0.25	1.26	2.37	
2.60	1.06	2.00	
2.94 (benzaldehyde)	0.53	0.99	29
4.42 (benzyl alcohol)	16.88	31.82	933
5.40	4.48	8.45	
7.13	18.26	34.41	

One other issue to consider is the efficiency of this distillation step. Table 2-13 summarizes the amounts of benzaldehyde and benzyl alcohol in each sample. Table 2-14 gives each of these masses as percentages of that in the original sample. Note how benzyl alcohol has more of a tendency to remain in the bottoms than benzaldehyde. This is due to benzyl alcohol having a boiling point of 205.2°C while benzaldehyde has a boiling point of 179.5°C (Lamer, 1996). In this boil-over step, about 74% of benzyl alcohol and 37% of benzaldehyde were recovered in a distillate (sum of Fractions A and B) half the volume of the original sample. Some benzaldehyde and benzyl alcohol are lost from this system due to possible side reactions such as oxidation to benzoic acid. This might be explained by the peak at 5.4 minutes which begins to show up in Fractions B and C (see Tables 2-11 and 2-12).

**Table 2-13: Mass Distribution of Benzaldehyde and Benzyl Alcohol During Boil-Over**

<u>Sample</u>	<u>Benzaldehyde Mass(g)</u>	<u>Benzyl Alcohol Mass (g)</u>
Original	0.0128	0.00768
A	0.00345	0.00231
B	0.00126	0.00341
C	4.35E-5	0.00140

**Table 2-14: Sample Masses as Percentages of Original Feed**

<u>Sample</u>	<u>Benzaldehyde</u>	<u>Benzyl Alcohol</u>
A	27.0	30.1
B	9.84	44.4
C	0.340	18.3

Part of the problem with the above experiment could have resulted from benzaldehyde and benzyl alcohol sticking to glassware. To test this, a much larger sample (100 mL) was completely boiled over. This sample consisted of regenerate combined from many different adsorption runs. A large feed size would dwarf any residual effects of glassware. Tables 2-15 and 2-16 give the respective GC profiles before and after boil-over.

**Table 2-15: 100 mL Regenerate Sample Before Boil-Over**

Retention Time (min)	Peak Area
0.18	0.744
2.97 (benzaldehyde)	49.5
4.44 (benzyl alcohol)	34.6
5.42	4.37
7.15	3.02
8.55	1.70
10.96	0.354
13.82	1.62

**Table 2-16: Regenerate Sample After Complete Boil-Over (Distillate)**

Retention Time (min)	Peak Area
0.17	2.12
2.96 (benzaldehyde)	46.7
4.45 (benzyl alcohol)	38.1
5.43	3.16
7.17	2.11

Note how the benzaldehyde peak area decreases by about 6% after boil-over. The benzyl alcohol concentration increases by 10% after boil-over. This fluctuation is within the range of normal variation for this GC. Nevertheless, the losses of benzaldehyde and benzyl alcohol from the system are significantly less than in the previous experiment. It should also be noted that the distillate has no color unlike the original regenerate which is brown.

While boil-over helps to separate out some of the heavier impurities, it is still desirable to isolate benzaldehyde and benzyl alcohol in more concentrated and pure forms. Since they both form azeotropes with water, distillation techniques are limited. Some experiments were consequently done in an attempt to extract these components into a more concentrated form. Ethyl acetate has shown some promising results.

An experiment was done with a sample of regenerate after boil-over. Table 2-17 gives the GC profile of this sample. 10 mL of ethyl acetate was added to this 100 mL sample. The mixture was shaken and allowed to separate into two liquid phases. The phase boundary was somewhat unclear because a viscous white emulsion was present at the boundary. The recovered ethyl acetate phase was about 2.5 mL in volume. The rest of it was dissolved into the water phase. Table 2-18 gives a GC profile of the ethyl acetate layer, and Table 2-19 gives a GC profile of the water layer. Ethyl acetate itself is present in the GC at 0.5 minutes. Notice how benzaldehyde (3 min) and benzyl alcohol (4.4 min) are respectively 14 and 11 times more concentrated in the ethyl acetate phase than in the original sample. Furthermore, the ethyl acetate phase is 64 and 15 times more concentrated with these two respective compounds than the water phase. However, note how some of the other components also prefer the ethyl acetate phase (e.g. 5.4 min). Also, the ethyl acetate phase takes on a brown color similar to that observed in the regenerate prior to boiling.

**Table 2-17: GC Profile of a 100 mL Regenerate Sample After Boil-Over**

Retention Time (min)	Peak Area
0.19	2.63
0.22	1.06
0.57	1.07
2.98 (benzaldehyde)	112
4.45 (benzyl alcohol)	40.7
5.43	3.03
7.16	2.40
10.98	1.10

**Table 2-18: Ethyl Acetate Phase of First Extraction**

Retention Time (min)	Peak Area
0.48	3638
3.08 (benzaldehyde)	1594
4.47 (benzyl alcohol)	464
5.43	41.5
7.15	14.6
10.97	1.06
11.53	3.40

**Table 2-19: Water Phase of First Extraction**

Retention Time (min)	Peak Area
0.49	551
2.95 (benzaldehyde)	25.1
4.43 (benzyl alcohol)	30.5
5.41	2.09

This is encouraging in light of the fact that 2.5 mL of ethyl acetate extracted 78% of the benzaldehyde from the 100 mL water phase. However, only 25% of the benzyl alcohol was removed from this water phase. These results show some logic in that benzyl alcohol is a more polar molecule, thus, preferring water as its solvent.

Since fair amounts of benzaldehyde and benzyl alcohol remained in the water phase after the first extraction, this 100 mL water phase was extracted again with 5 mL of ethyl acetate. This time, none of the ethyl acetate was lost to the water phase as it was already saturated. Tables 2-20 and 2-21 show the respective ethyl acetate and water layers after extraction. Note how the ethyl acetate phase is 47 and 13 times more

concentrated in benzaldehyde and benzyl alcohol respectively. This extraction removed 51% and 25% of these two respective compounds from the water phase as can be seen by the differences in Tables 2-19 and 2-21.

**Table 2-20: Ethyl Acetate Layer after Second Extraction**

Retention Time (min)	Peak Area
0.48	1272
0.53	2519
3.05 (benzaldehyde)	575
4.49 (benzyl alcohol)	299
5.46	22.3

**Table 2-21: Water Layer after Second Extraction**

Retention Time (min)	Peak Area
0.49	596
2.94 (benzaldehyde)	12.2
4.43 (benzyl alcohol)	22.9
5.42	1.42

Since ethyl acetate is more volatile than the aromatic compounds of interest, a distillation was done on a mixed sample of the ethyl acetate layers from Tables 2-18 and 2-20. A 4.5 mL sample was used for this test, and the GC profile is given in Table 2-22. Once again, ethyl acetate accounts for the peaks near 0.5 minutes. This experiment involved boiling off the ethyl acetate while monitoring the benzaldehyde and benzyl alcohol concentrations in the bottoms. Readings were taken when 1 mL (Table 2-23) and 0.2 mL (Table 2-24) of solution were left in the feed pot. Note that, in Table 2-24, the benzaldehyde peak area was split between 3.13 and 3.21 minutes, probably due to a bad injection. When the 4.5 mL sample is distilled down to 1 mL, benzaldehyde becomes about 5.6 times more concentrated and benzyl alcohol becomes 5.93 times more concentrated. These numbers would seem to imply that a chemical reaction is producing more of each of these chemicals since we would expect the solution to be no greater than

4.5 times more concentrated with each of these chemicals if no reaction were occurring. However, we are not completely certain whether the GC area is a linear function of concentration in these concentration ranges. When the 1 mL bottoms is distilled down to 0.2 mL, benzaldehyde and benzyl alcohol show 1.4-fold and 1.6-fold peak area increases respectively. It appears that the aromatics begin boiling off at about this point.

**Table 2-22: Ethyl Acetate Solution to be Distilled**

Retention Time (min)	Peak Area
0.48	1627
0.51	2203
3.05 (benzaldehyde)	1084
4.46 (benzyl alcohol)	387
5.42	34.0
7.13	12.4
11.5	2.94

**Table 2-23: GC of 1 mL Bottoms**

Retention Time (min)	Peak Area
0.48	2158
3.19 (benzaldehyde)	6043
4.52 (benzyl alcohol)	2295
5.45	241
7.11	100

**Table 2-24: GC of 0.2 mL Bottoms**

Retention Time (min)	Peak Area
0.48	597
3.13 (benzaldehyde)	4670
3.21 (benzaldehyde)	3702
4.53 (benzyl alcohol)	3707
5.30	247
5.44	348
7.06	300

It should be noted that the product is a dark brown color at this stage. As was previously noted, this color first reappeared after the ethyl acetate extractions. This seems to imply that some of the heavier components have not been completely separated

out in this sequence of extraction and distillation steps. Nevertheless, Table 2-24 represents the best product that the current techniques are able to yield.

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# **Chapter 3: ADSORPTION MODELING WITH THE ESD EQUATION OF STATE**

*By  
Aaron D. Soule, Cassandra A. Smith, and Carl T. Lira*

## **ABSTRACT**

The simple local density approach (SLD) is used to extend the ESD (Elliott et al., 1990) equation of state to the modeling of gas adsorption on activated carbon, providing significant improvement in quantitative modeling compared to the SLD approach using the Peng-Robinson equation of state (Chen et al., 1997) or the van der Waals equation (Rangarajan et al., 1995). Compared to the Peng-Robinson and van der Waals equations, the ESD more accurately represents the contributions of attractive and repulsive forces, and therefore provides increased accuracy when the attractive term is modified for adsorption. Isotherms are represented for nine fluids on three different activated carbons using temperature-independent parameters over temperature ranges of up to 167 K. The fluid-solid interaction energies are shown to correlate with the fluid Lennard-Jones parameter.

# INTRODUCTION

Adsorption is a topic which has been treated by a variety of models. Monte Carlo simulations and molecular dynamics are computationally intensive methods for calculating adsorption. Engineers often desire efficient methods for obtaining good approximations. The best methods incorporate as few adjustable parameters as possible. The Langmuir, Toth, and Freundlich models are easy to fit, but require temperature-dependent parameters. The simplified local density (SLD) approach is an engineering method that can be used with any equation of state and offers predictive capability with only two temperature-independent adjustable parameters. This paper focuses on results obtained with the ESD equation of state.

Previous studies have focused on adsorption modeling with the simplified local density approach applied to the van der Waals (Rangarajan et al., 1995) and Peng-Robinson (Chen et al., 1997) equations of state. These equations, while showing some strengths, have characteristics which limit their ability to model fluid properties. For example, the van der Waals equation is the most simple cubic equation and offers only qualitative prediction. The Peng-Robinson, on the other hand, represents adsorption accurately on flat surfaces. It is quite effective in modeling the adsorption of supercritical fluids such as ethylene. It is capable of predicting the isotherm crossovers found in experimental data. In porous materials, some success has been obtained (Chen et al., 1997), but the general application to porous materials cannot generally fit both the Henry's law region and the adsorbent capacity. Further, when fitting data, it is difficult to maintain good fits with the same parameters over large temperature ranges.

The ESD is also a cubic equation of state, however, it's theoretical grounding is superior in that the repulsive term is constructed to match computer simulations of spheres and chains using a scalar shape factor to account for deviations from spherical geometry. The attractive term consists of an expression for the spherical square-well potential coupled with a shape factor correction. The improved subdivision of repulsive and attractive forces is important for the SLD approach, which leads to the greater accuracy of adsorption modeling.

## SIMPLIFIED LOCAL DENSITY MODEL USING ESD

The Elliott, Suresh, Donohue (ESD) equation of state (Elliott et al., 1990) consists of repulsive and attractive terms which are weighted differently than those in the Peng-Robinson equation of state. The ESD equation takes the form  $Z=1+Z^{rep}+Z^{atr}$ , where

$$Z^{rep} = \frac{4c\eta}{1-1.9\eta} \quad (3-1)$$

$$Z^{atr} = \frac{9.5q\eta Y}{1+1.7745 < \eta Y >} \quad (3-2)$$

Here,  $c$  is a shape factor for the repulsive term,  $q$  is a shape factor for the attractive term,  $\eta$  is the reduced density ( $\eta=b\rho$ ),  $b$  is the component's size parameter,  $\rho$  is the density,  $Z$  is compressibility, and  $Y$  is a temperature-dependent attractive energy parameter.

Although the ESD equation also can represent associating fluids, none of the components presented in this paper have associative characteristics, so the terms are omitted from this paper. The equation can also be represented in terms of fugacity as follows.

$$\ln f_{calc} = -\frac{4}{19}c \ln(1-1.9\eta) + \frac{4c\eta}{(1-1.9\eta)} - \frac{9.5q}{1.7745} \ln(1+1.7745 < Y\eta >) - \frac{9.5qY\eta}{(1+1.7745 < Y\eta >)} - \ln \frac{V}{RT} \quad (3-3)$$

$V$  is the molar volume,  $T$  is temperature,  $R$  is the ideal gas constant, and  $f_{calc}$  is fugacity.

In the slit-shaped pores used in modeling, the fluid-solid interaction potential was modeled using the same 10-4 potential as in previous work (Chen et al., 1997), incorporating five carbon layers in the form of:

$$\Psi_1(z) = 4\pi\rho_{atoms}\sigma_{fs}^2\epsilon_{fs} \left\{ \begin{array}{l} \frac{0.2}{Eta^{10}} - \frac{0.5}{Eta^4} - \frac{0.5}{(Eta + \alpha)^4} \\ - \frac{0.5}{(Eta + 2\alpha)^4} - \frac{0.5}{(Eta + 3\alpha)^4} - \frac{0.5}{(Eta + 4\alpha)^4} \end{array} \right\} \quad (3-4)$$

where  $\alpha$  is the plane spacing between the solid particles ( $3.35\text{\AA}/\sigma_{fs}$ ),  $\sigma_{fs}$  is the average of the fluid and solid molecular diameters [ $\sigma_{fs} = (\sigma_{ff} + \sigma_{ss}) / 2$ ],  $z$  is the particle position in the slit relative to the carbon surface,  $Eta = (z + \sigma_{ss}) / \sigma_{fs}$  is the dimensionless distance from the carbon centers in the first plane, and  $\rho_{atoms}$  represents the number of carbon-plane atoms per square Angstrom ( $0.382 \text{ atoms}/\text{\AA}^2$ ). The fluid-solid potential in relation to the second wall,  $\Psi_2(z)$ , can be calculated by replacing  $Eta$  in equation 3-4 with  $Xi$ , which is the distance from the second wall (angstroms) divided by the fluid-solid diameter (see Figure 3-1). The total potential is expressed as

$$\Psi_T = \Psi_1 + \Psi_2 \quad (3-5)$$

The thermodynamic constraints of the adsorbing fluid fugacity can be estimated by using equations 3-6 through 3-8 below (Chen et al., 1997).

$$\mu_{bulk} = \mu_{ff}(z) + \mu_{fs}(z) \quad (3-6)$$

$$\mu_{ff}(T) = \mu^\circ(T) + RT \ln \left[ \frac{f_{ff}(z)}{f^\circ} \right] \quad (3-7)$$

$$\mu_{bulk}(T) = \mu^\circ(T) + RT \ln \left[ \frac{f_{bulk}}{f^\circ} \right] \quad (3-8)$$

The local chemical potential due to fluid-fluid interactions,  $\mu_{ff}$ , is calculated assuming that the local fluid-fluid fugacity can be estimated using the fluid-solid potential,  $\Psi_T$ , and the bulk fluid fugacity,  $f_{bulk}$ . In these equations  $\mu_{bulk}$  is the bulk chemical potential,  $f^\circ$  and  $\mu^\circ$  are the standard state fugacity and chemical potential respectively, and  $\mu_{fs}$  is the fluid-solid contribution to the chemical potential. Note that  $\mu_{ff}$  and  $f_{ff}$  (fugacity) are functions of  $z$  (position).

$$f_{ff}(z) = f_{bulk} \exp\left[\frac{-\Psi_T(z)}{kT}\right] \quad (3-9)$$

For previous work with the Peng-Robinson equation, algebraic expressions were developed for the Peng-Robinson attractive equation of state parameter,  $a(z)/a_{bulk}$  (Chen et al., 1997). The same expressions are used to calculate the ESD  $Y(z)/Y_{bulk}$  as for the Peng-Robinson  $a(z)/a_{bulk}$  based on these previous derivations. Thus, in slits, the local fluid-fluid chemical potential (fugacity) is predicted based on  $Y(z)$  which can be determined from  $Y_{bulk}$  and the published algebraic expression for  $Y(z)/Y_{bulk}$ .

In previous work, fluid closer to the wall than  $Eta=0.5$  or  $Xi=0.5$  (half the diameter of a fluid particle) was ignored (Chen et al., 1997), assuming that no molecular centers could be contained in this area. This manuscript assumes that the density cutoff should be the point where the local fugacity,  $f_{ff}$ , is one tenth of a percent of the bulk fugacity,  $f_{bulk}$ . This yields a more realistic density profile near the wall. From Equation 3-8, one can calculate  $\Psi(z)/k$  as approximately 2500 K when  $f_{ff}(z)/f_b=0.001$  at 373 K. This value is used for each temperature calculation, which makes the cutoff distance dependent on the slit width only. This is merely an approximation, but the density below this region is always low in all calculations we have checked. For the density calculations in the region  $Eta<0.5$  or  $Xi<0.5$ , we use  $Y(z)/Y_{bulk}=0.5$ .

The local density is obtained at each  $z$  by using equations (3-3), (3-5), and (3-9). The difference between the local and bulk densities is integrated in the correct geometric form over the slit distance using the modified Simpson's rule to yield excess,  $\Gamma^{ex}$ .

$$\Gamma^{ex} = A \int [\rho(z) - \rho_{bulk}] dz \quad (3-10)$$

The variable  $A$  is the surface area per unit weight of adsorbent (e.g., square meters per gram). In the case of adsorption in a slit with homogeneous parallel walls, this integration over the entire slit width is divided by two since two walls contribute to the surface area of a slit.

For each fit discussed in this paper, the value of  $A$  was taken from the cited reference and not used as an adjustable parameter in the model. The values of  $\sigma_{ff}$  are tabulated Lennard-Jones diameters of each fluid, and  $\sigma_{ss}$  is the reported diameter of carbon (Reid et al., 1987). In calculating adsorption in slits, two adjustable temperature-independent parameters were fitted:  $\epsilon_{fs}/k$  (fluid-solid interaction potential in Kelvin) and  $H$  (slit width in angstroms). The parameters were fit to optimize the simultaneous representation of all data in a given figure rather than optimization of individual isotherms.

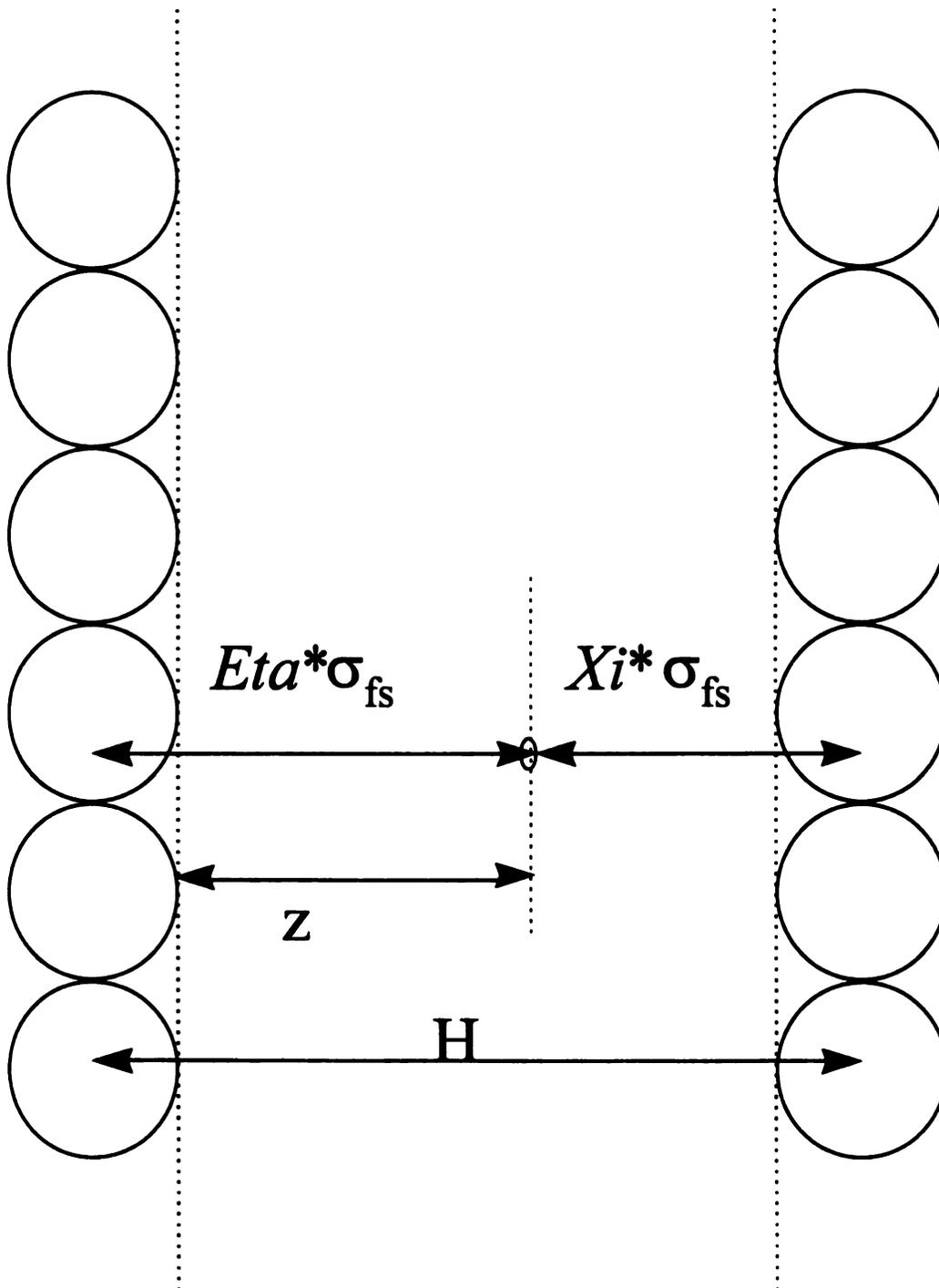


Figure 3-1: Model of a slit-shaped pore showing the variables used to define distances in the manuscript;  $\text{Eta} = (z + \sigma_{ss})/\sigma_{fs}$ ,  $\text{Xi} = (H - \text{Eta} * \sigma_{ss})/\sigma_{fs}$

## RESULTS AND DISCUSSION

Several sets of pure component adsorption data have been successfully fitted with the ESD version of the simplified local density model. Table 3-1 lists the pure component ESD parameters, all of which are obtained from bulk fluid properties. Figure 3-2 shows the adsorption of ethylene on BPL carbon over 167 K. Figure 3-3 shows ethane adsorption which is also a good fit over 167 K. Other fits include butane over 110 K (Figure 3-4), propane over 167 K (Figure 3-5), methane over 89 K (Figure 3-6), propylene over 139 K (Figure 3-7) and nitrogen over 111 K (Figure 3-8). It is important to note that all these fits were performed by simultaneously optimizing all of the isotherms in a given graph through adjustment of the two parameters. In the cases of butane and propylene, it seems as though the model has trouble fitting low pressure data. Better fits seem to be generated when the pressure ranges are wider. Nitrogen shows inaccurate predictions of temperature dependence. The fit of propane is weak in that, at the highest temperature, the knee region is overpredicted. While butane, propylene, and propane deviate significantly from the sphericity assumption of the model, it is not known why the nitrogen data are not fit more precisely. Figures 3-9 and 3-10 show that the model can also represent acetylene and carbon monoxide.

**Table 3-1: Pure Component ESD Parameters**

Component	c	q	$\epsilon_{ff}/k$ (K)	b (cm <sup>3</sup> /mole)
acetylene	1.6808	2.2967	190.510	13.053
butane	1.7025	2.338	260.583	29.039
carbon monoxide	1.2367	1.4509	103.784	10.171
ethane	1.3552	1.6765	220.449	16.716
ethylene	1.305	1.581	210.275	15.013
methane	1.0382	1.0728	178.082	10.863
nitrogen	1.1433	1.273	106.155	9.907
propane	1.5481	2.0441	241.433	22.921
propylene	1.5142	1.9794	241.896	20.890

There is a correlation between the pure fluid Lennard-Jones parameters and fluid-solid interaction energy parameters. Figures 3-11 and 3-12 graphically demonstrate this relationship for Columbia Grade L and BPL carbons respectively. The fluid-solid parameters do show some variation between different activated carbons for the same component. This effect is more pronounced for some components than for others, but in the case of this study, the parameters do not vary more than 10 K for a single component.

When examining the ESD equation of state, it is also important to consider the validity of the bulk properties. Since the adsorbed phases have liquid-like densities, the representation of liquid molar volumes is important. Table 3-2 gives some saturation bulk property comparisons between the Peng-Robinson and ESD equations near each component's critical temperature. This particular sample of bulk properties was chosen to give the reader a general perspective on the performance of the ESD as compared to experimental data and the Peng-Robinson equation of state. Since temperature and pressure are specified, molar volume is the dependent variable used for comparison. While the ESD appears to predict gas volumes better than the Peng-Robinson, the ESD is weaker in predicting liquid properties. As can be seen in the data, the ESD volumes vary

from experimental volumes by 20% or more for liquids. Gas volumes vary by up to 10 %. The ability of the ESD to more accurately model adsorption over wide temperature ranges is attributed to the superior representation of the individual contributions of attractive and repulsive forces, since the bulk liquid properties are predicted with about the same or less accuracy.

**Table 3-2: Comparison of experimental saturation molar volumes (Starling, 1973) to the bulk Peng-Robinson and bulk ESD predictions. All data points are near the critical temperature.**

	Temperature (K)	Reduced Temp.	Pressure (MPa)	Experimental cm <sup>3</sup> /gmol	Peng-Robinson cm <sup>3</sup> /gmol	ESD cm <sup>3</sup> /gmol
Methane (L)	188.7	0.99	4.32	70.12	83.30	91.84
(G)				162.51	153.74	160.48
Ethane (L)	302.6	0.99	4.62	102.44	121.00	134.00
(G)				235.98	217.18	231.33
Propane (L)	363.7	0.98	3.81	143.94	155.28	175.33
(G)				368.35	356.55	382.21
N-Butane (L)	422	0.99	3.62	213.63	219.00	247.39
(G)				371.86	379.11	414.71
Ethylene (L)	277.6	0.98	4.51	86.88	101.23	113.41
(G)				240.70	231.54	245.65
Propylene (L)	360.9	0.99	4.29	131.62	152.18	172.04
(G)				300.22	298.49	321.69
Nitrogen (L)	124.8	0.99	3.17	63.80	74.36	81.28
(G)				146.31	140.28	147.06

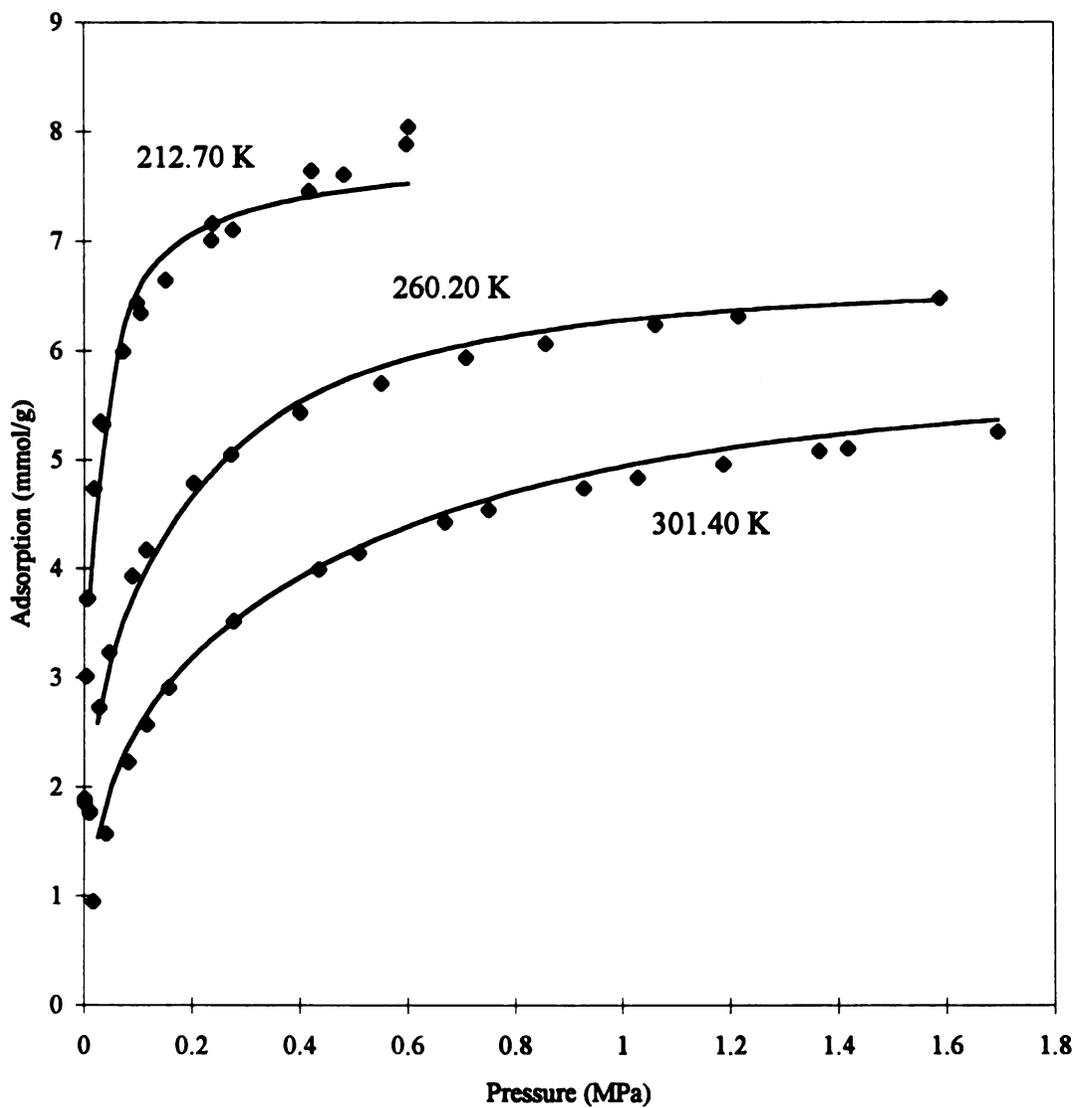


Figure 3-2A: Adsorption of ethylene on BPL activated carbon (988 square meters per gram) where  $H=13.7$  angstroms and  $\epsilon_p/k=103$  K. Data of Reich, et al., 1980.

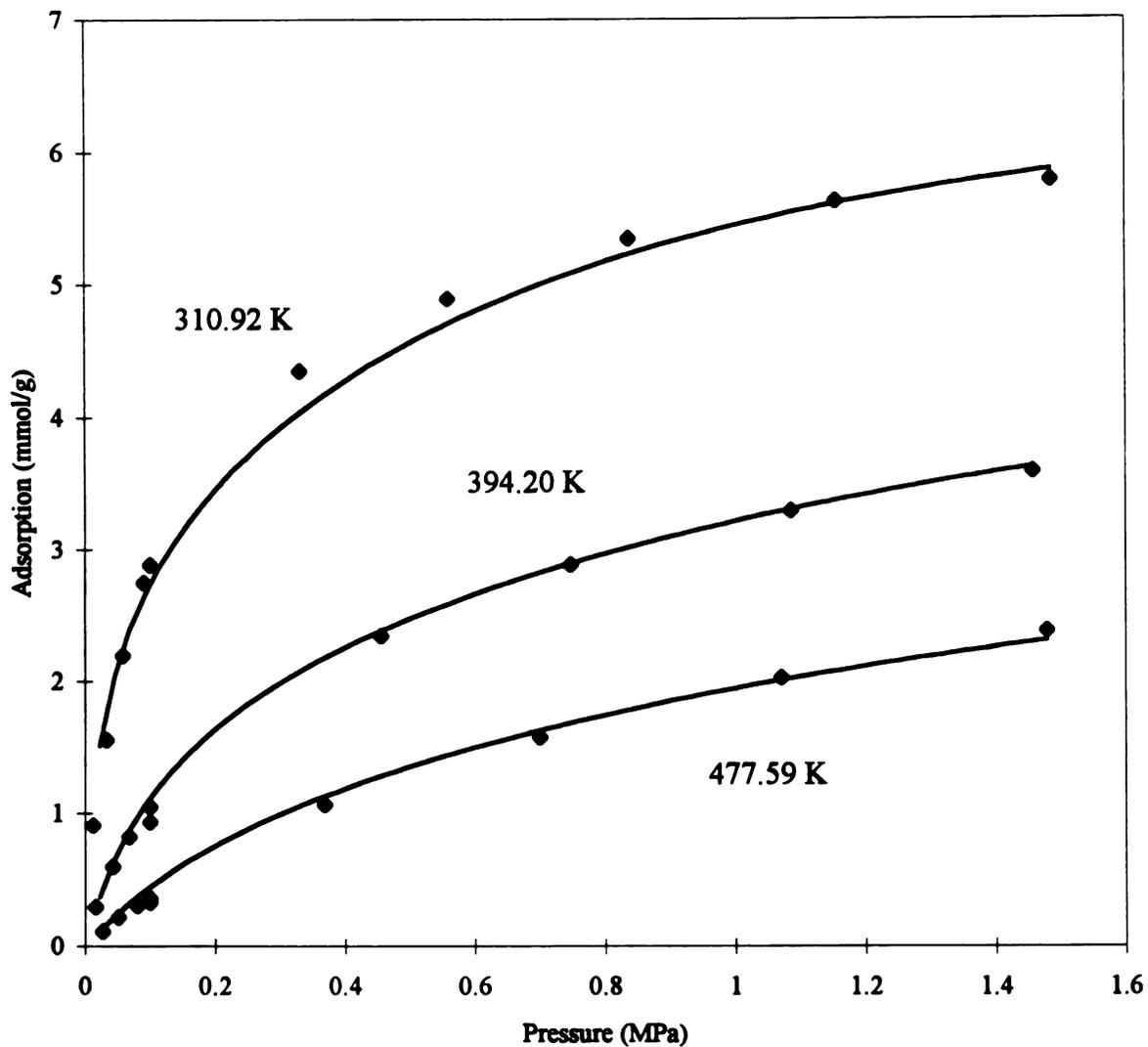


Figure 3-2B: Adsorption of ethylene on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=13.7$  angstroms and  $\epsilon_r/k=104$  K. Data of Ray and Box, 1950.

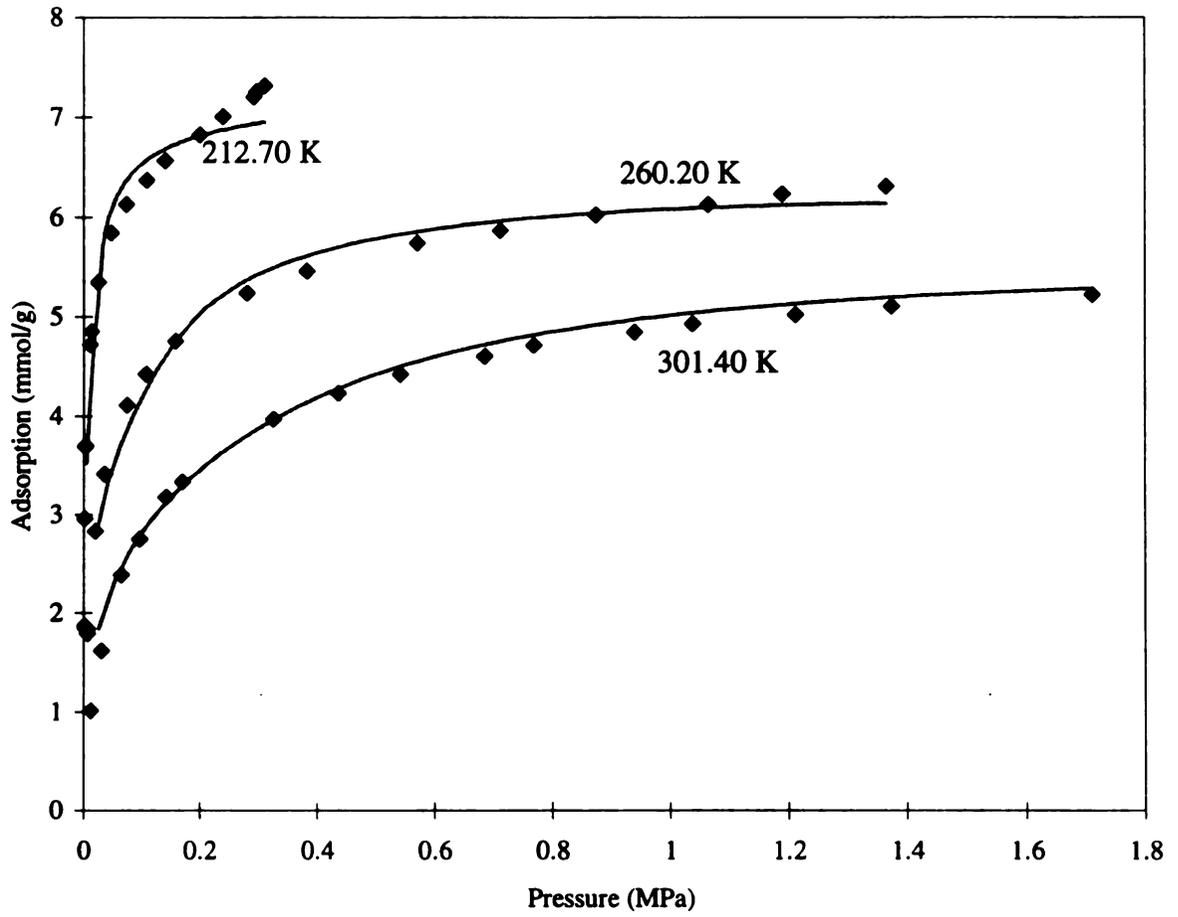


Figure 3-3A: Adsorption of ethane on BPL activated carbon (988 sq. meters per gram) where  $H=14.2$  angstroms and  $\epsilon_{tr}/k=102$  K. Data of Ray and Box, 1950.

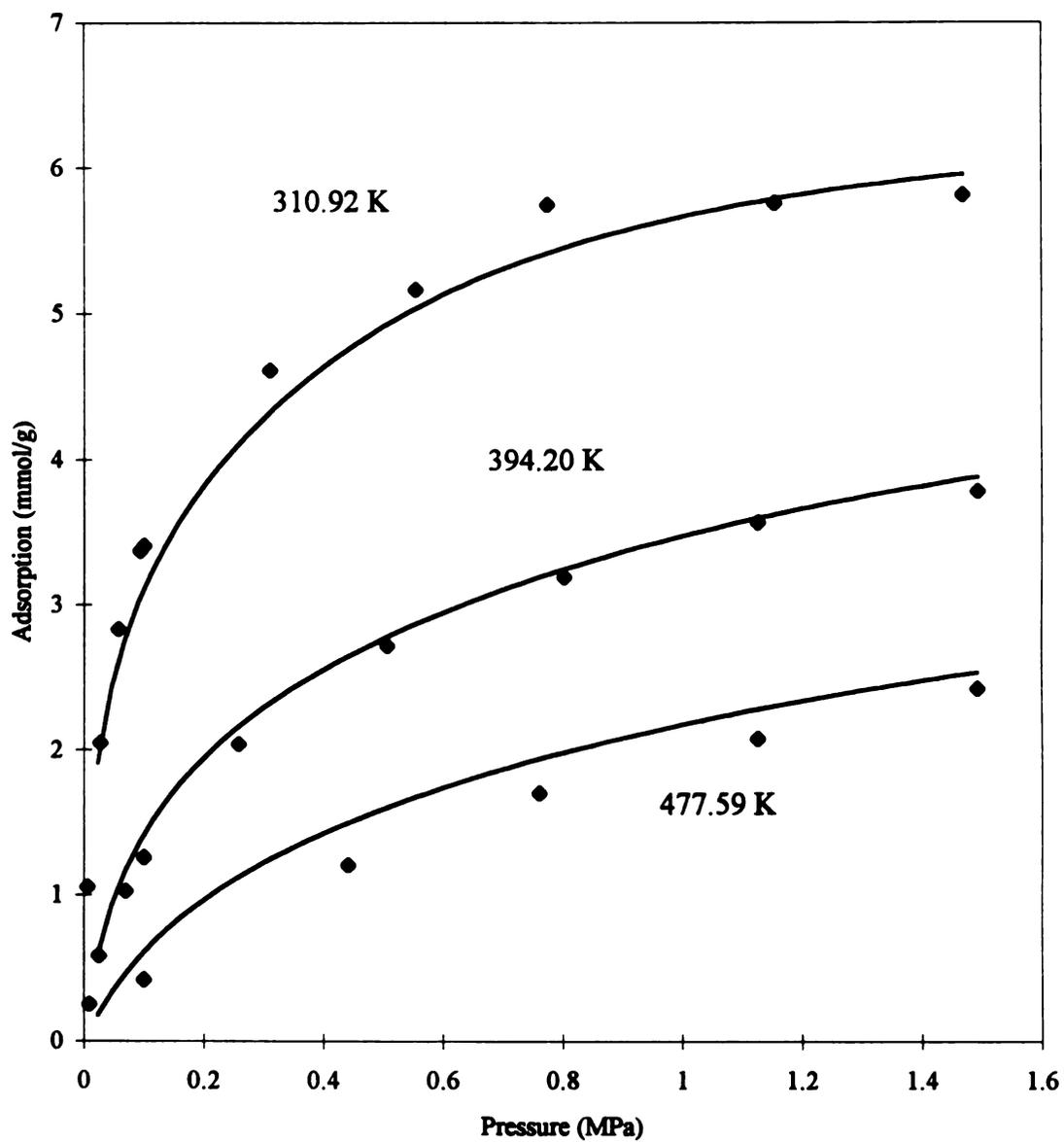


Figure 3-3B: Adsorption of ethane on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=14.3$  angstroms and  $\epsilon_p/k=104$  K. Data of Ray and Box, 1950.

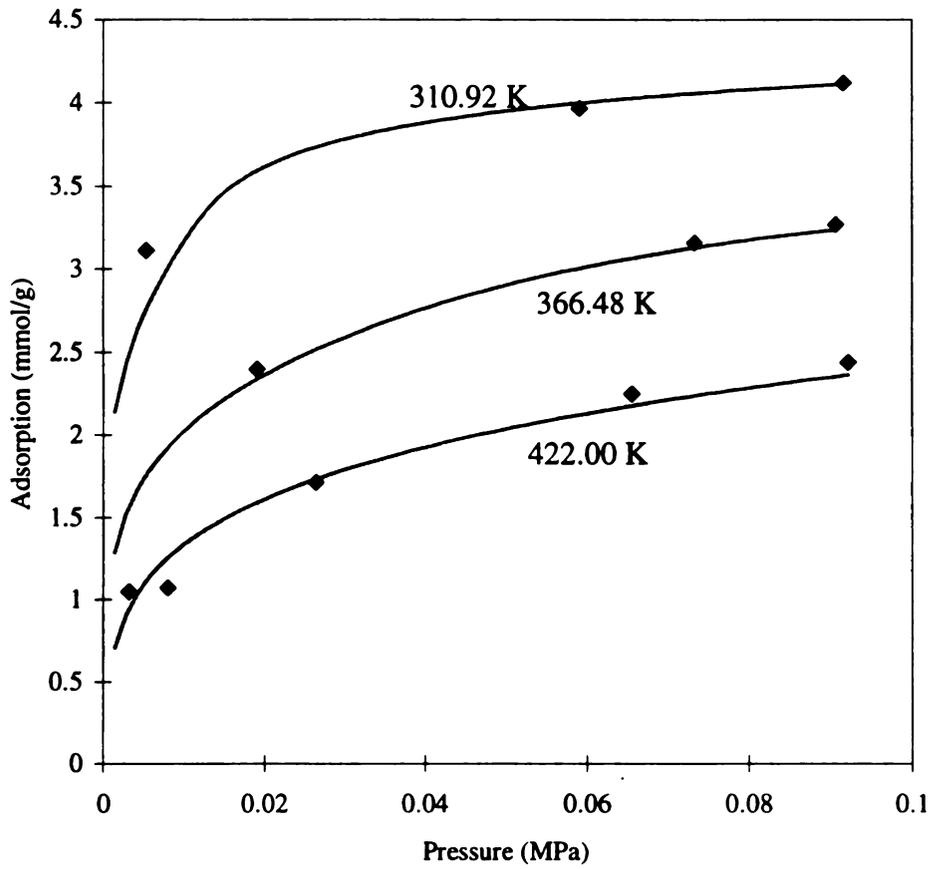


Figure 3-4: Adsorption of butane on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=14.1$  angstroms and  $\epsilon_{ts}/k=160$  K. Data of Ray and Box, 1950.

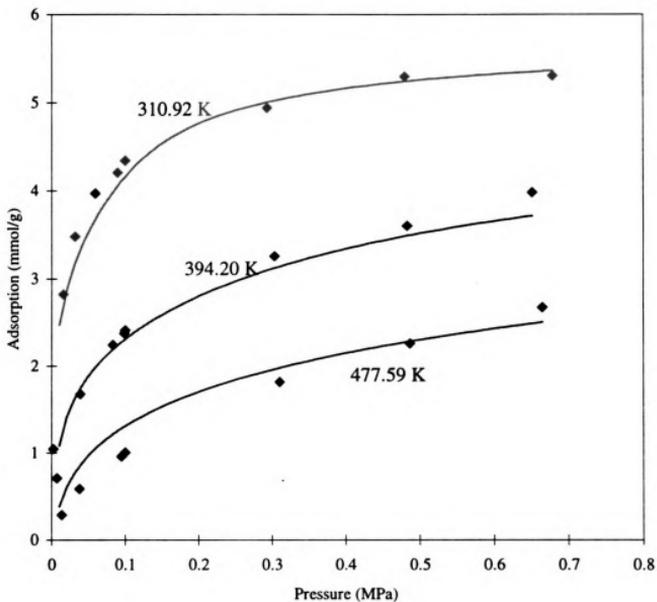


Figure 3-5: Adsorption of propane on Columbia Grade L activated carbon (1152 sq. meters per gram) where  $H=15.6$  angstroms and  $\epsilon_0/k=114$  K. Data of Ray and Box, 1950.

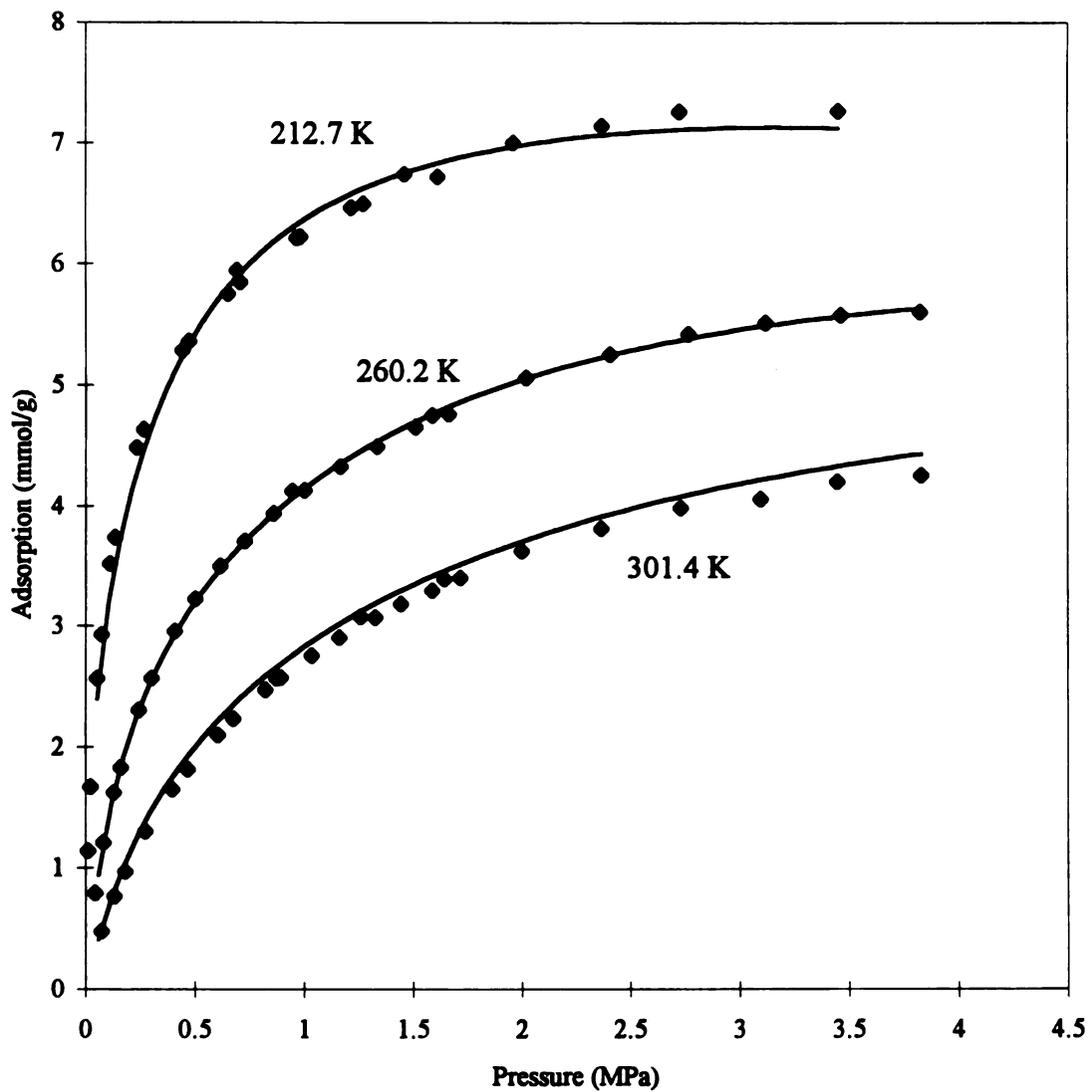


Figure 3-6: Adsorption of methane on BPL activated carbon (988 sq. meters per gram) where  $H=12.1$  angstroms and  $\epsilon_s/k=73$  K. Data from Reich, et. al., 1980.

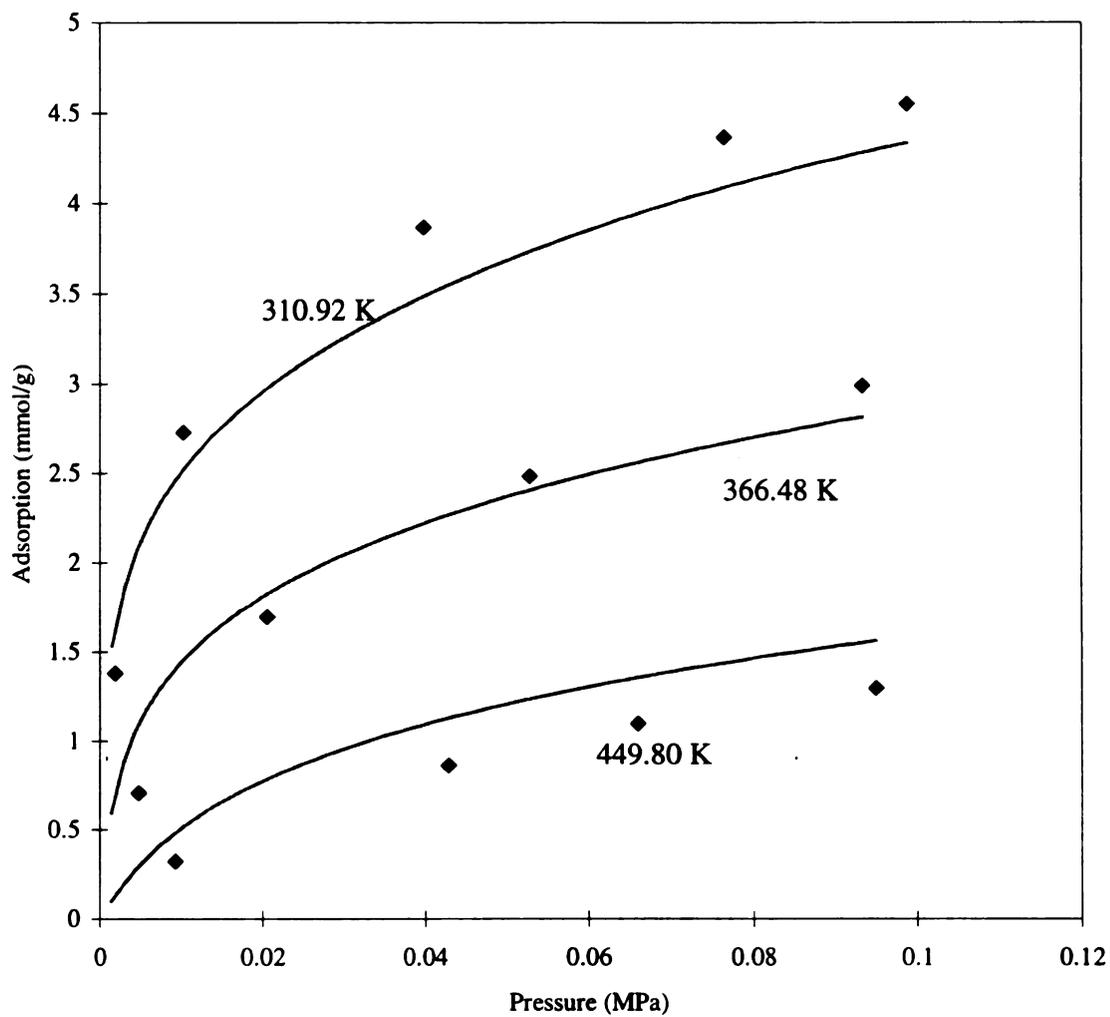


Figure 3-7A: Adsorption of propylene on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=14.3$  angstroms and  $\epsilon_{fs}/k=126$  K. Data of Ray and Box, 1950.

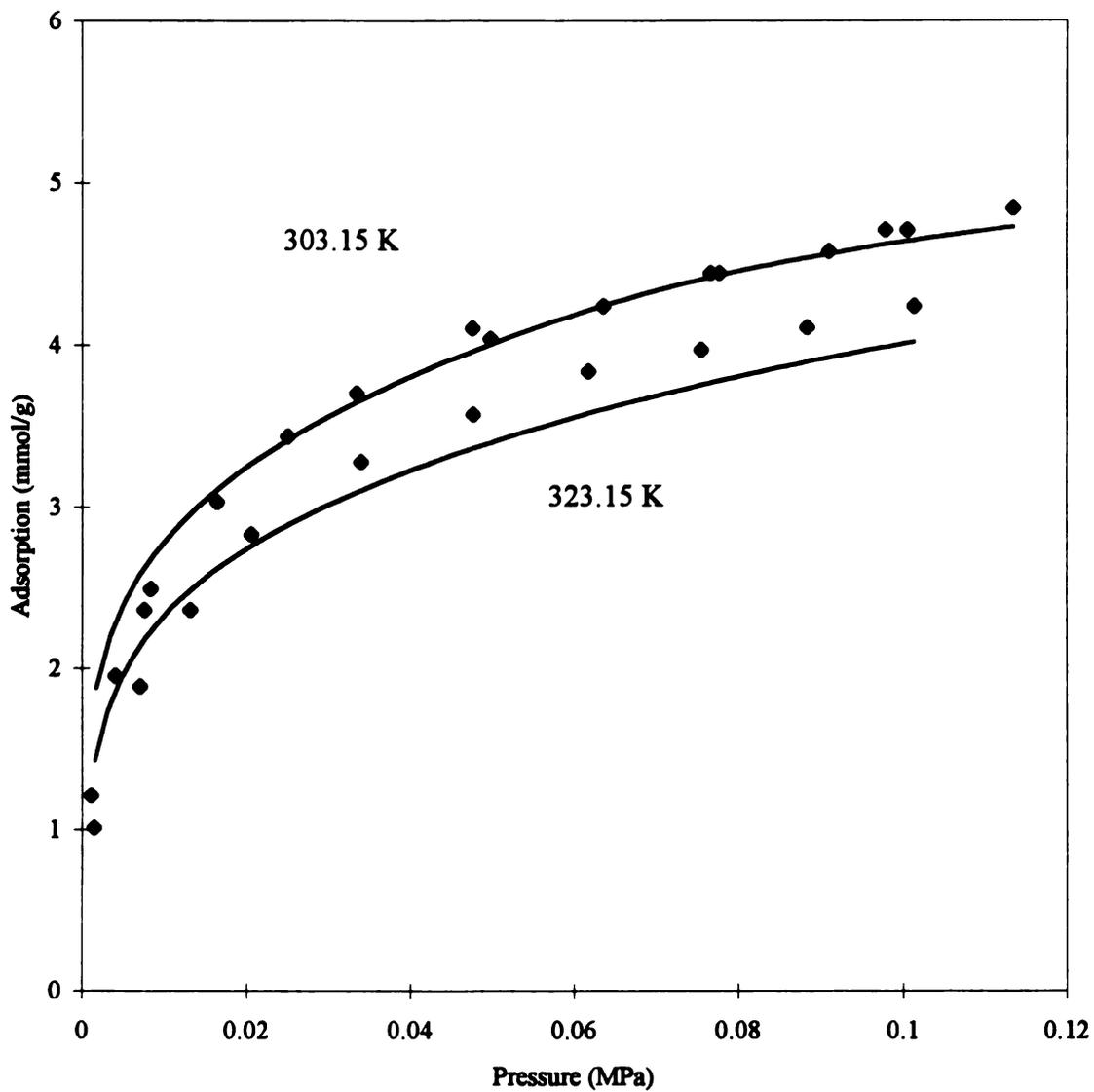


Figure 3-7B: Adsorption of propylene on BPL activated carbon (1050-1150 sq. meters per gram) where  $H=14.3$  angstroms and  $\epsilon_{\text{tr}}/k=132$  K. Data of Laukhuf, et al., 1969.

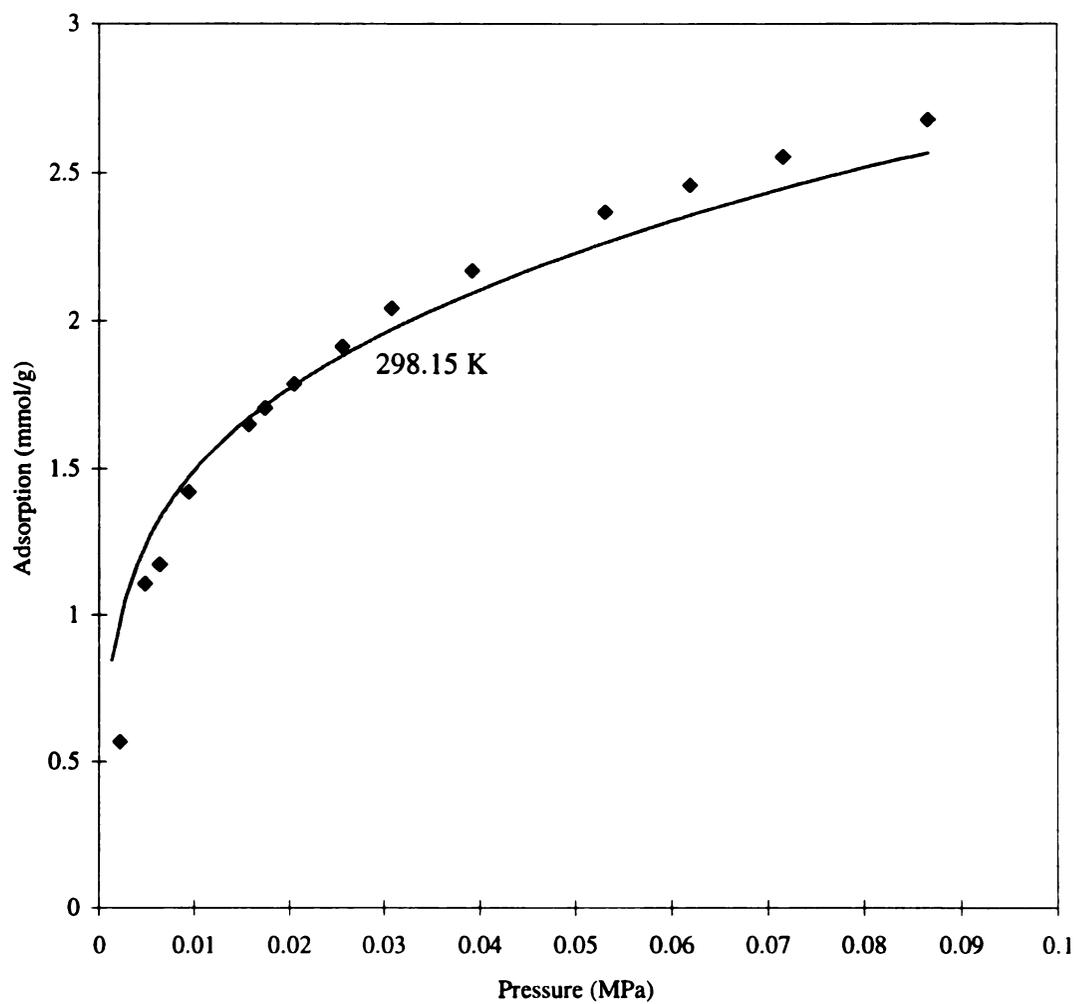


Figure 3-7C: Adsorption of propylene on Black Pearls I carbon (705 sq. meters per gram) where  $H=14.0$  angstroms and  $\epsilon_s/k=115$  K. Data of Lewis, et al., 1950.

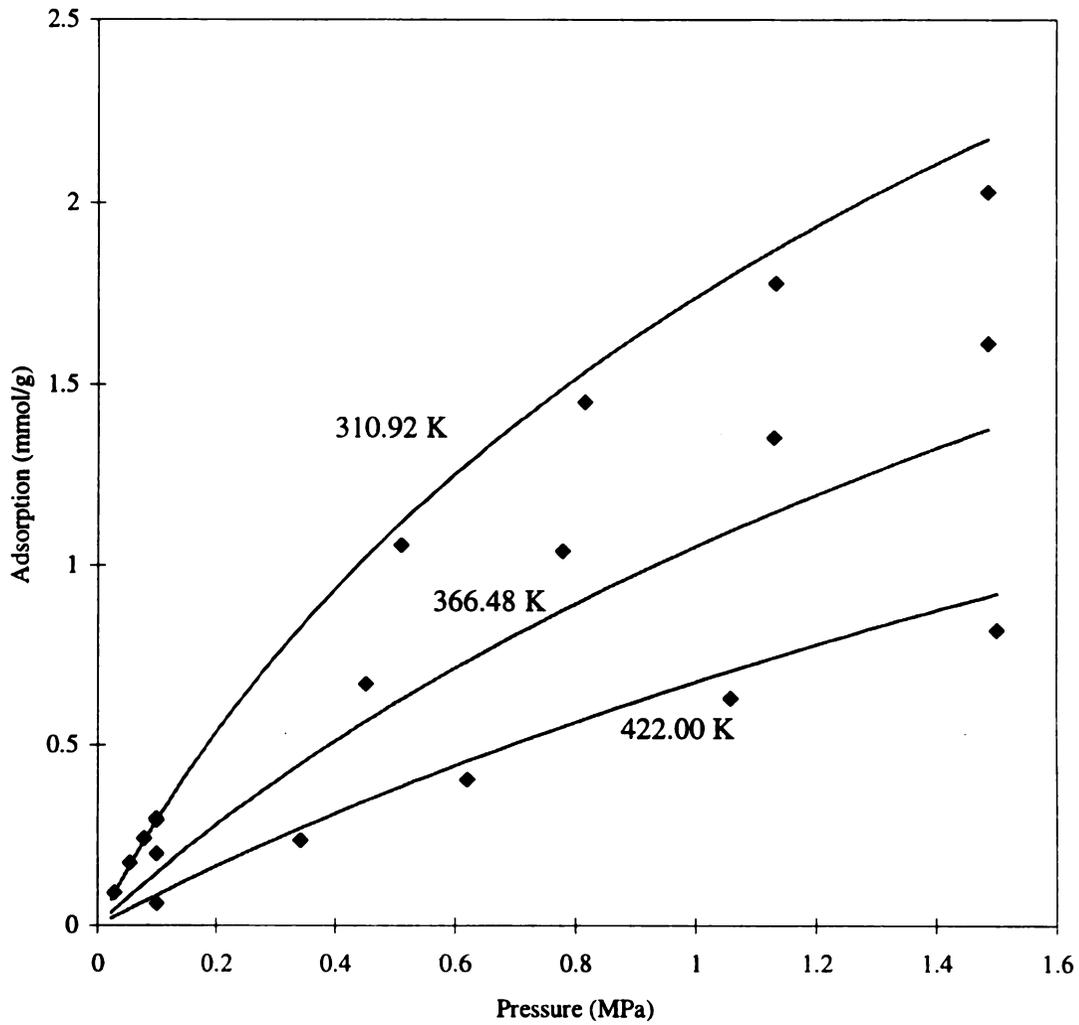


Figure 3-8: Adsorption of nitrogen on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=12.6$  angstroms and  $\epsilon_s/k=60$  K. Data of Ray and Box, 1950.

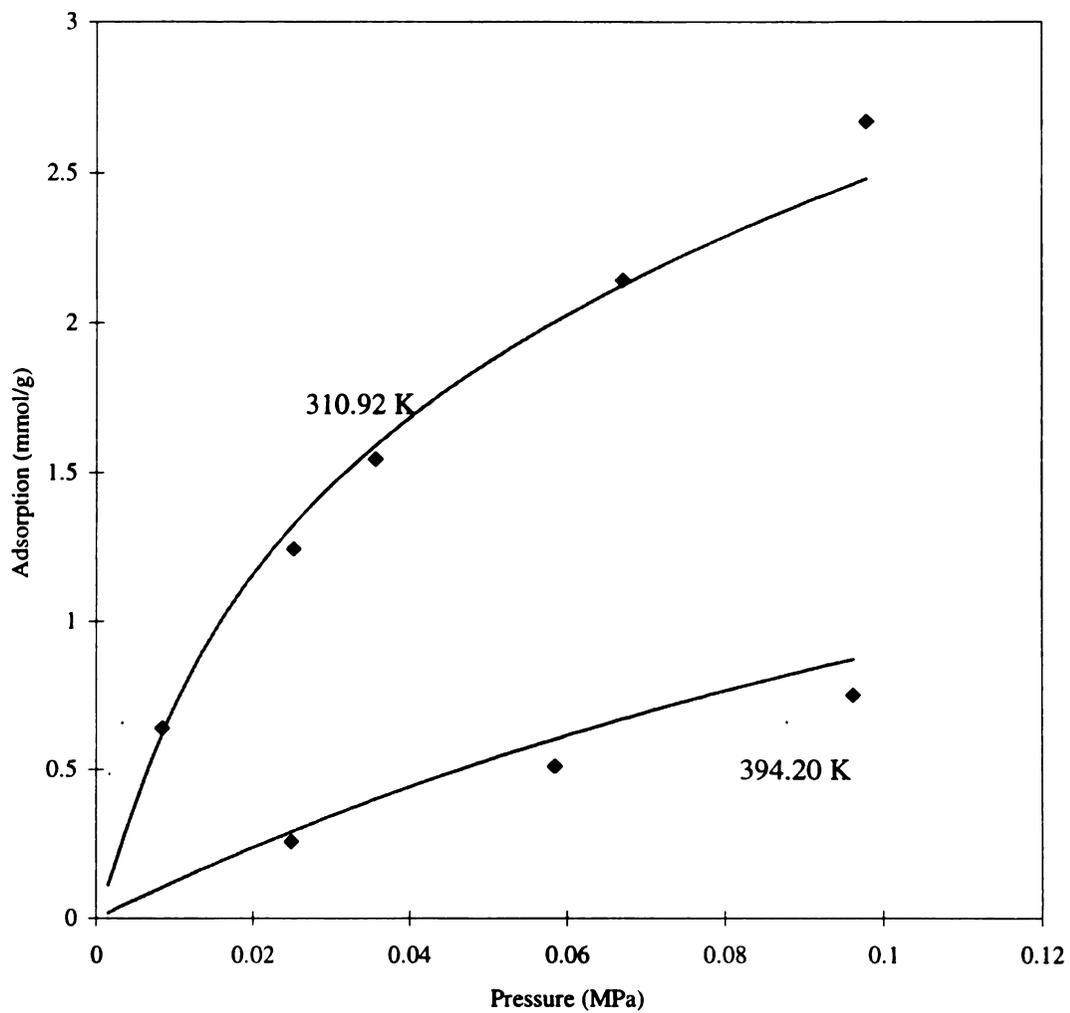


Figure 3-9: Adsorption of acetylene on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=14.5$  angstroms and  $\epsilon_{is}/k=103$  K. Data of Ray and Box, 1950.

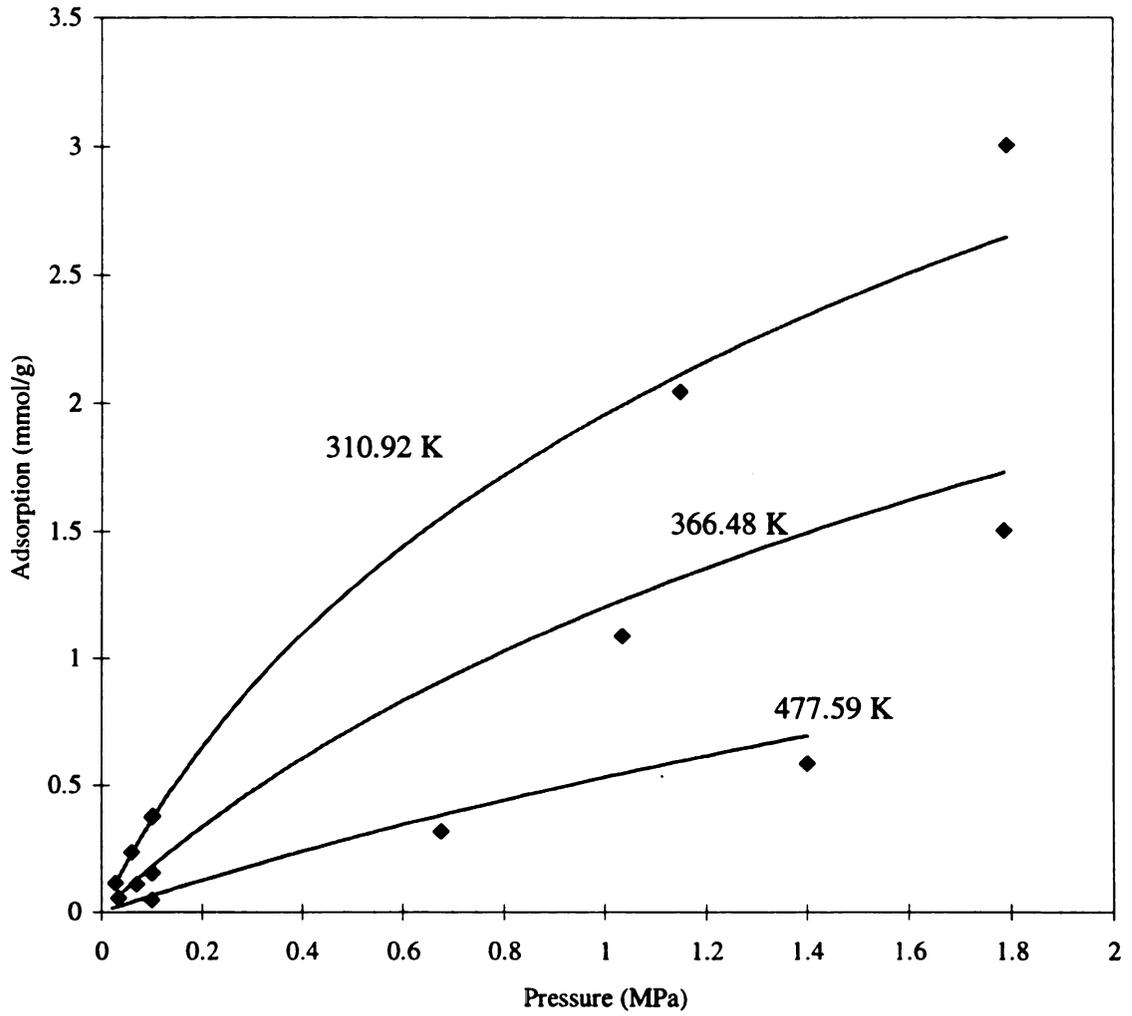


Figure 3-10: Adsorption of carbon monoxide on Columbia Grade L carbon (1152 sq. meters per gram) where  $H=15.8$  angstroms and  $\epsilon_{fs}/k=70$  K. Data of Ray and Box, 1950.

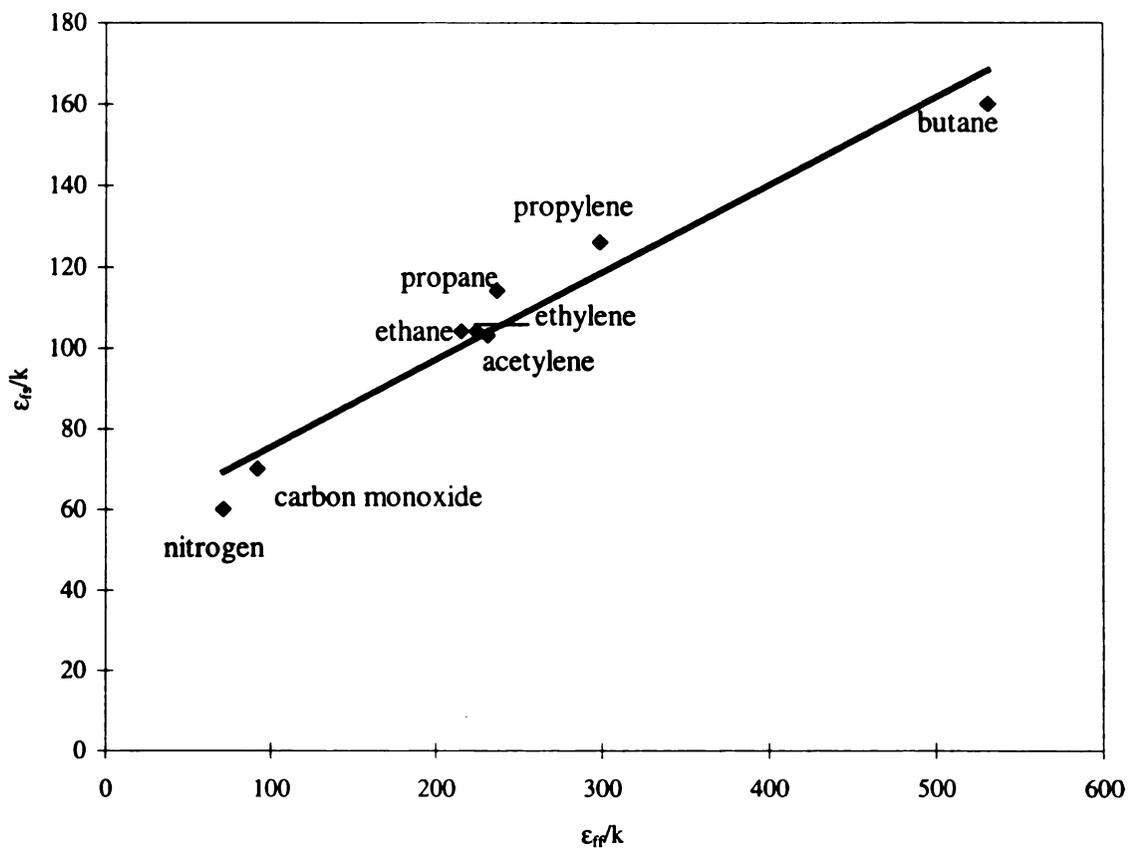


Figure 3-11: Correlation of fluid-solid and fluid-fluid interaction potentials. Fluid-fluid parameters from Reid, Prausnitz, and Poling, 1987. Columbia Grade L carbon.

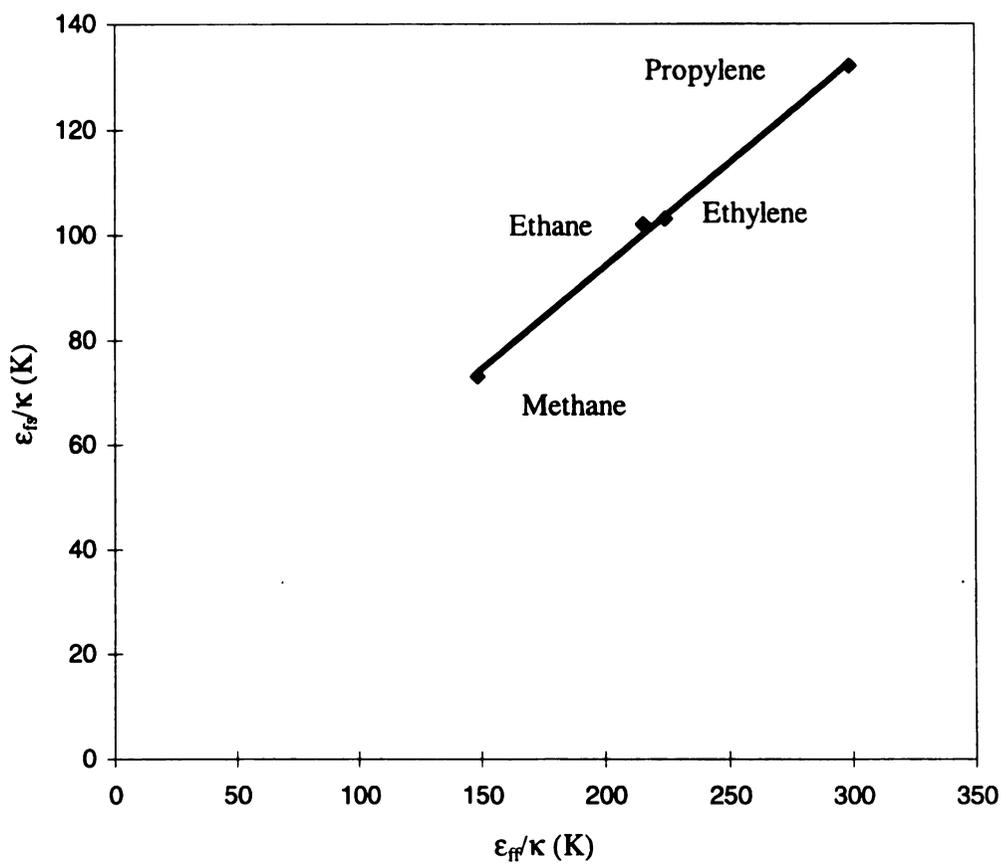


Figure 3-12: Correlation of fluid-fluid and fluid-solid interaction potentials. Fluid-fluid parameters from Reid, Prausnitz, and Poling, 1987. BPL carbon.

## **SUMMARY**

This paper has shown that the ESD equation of state can be adapted for successful adsorption modeling. While nitrogen and the higher molecular weight components presented in this paper can't be fitted as well as others, it is important to note that good engineering approximations can still be made with any of these compounds.

Our goal is to fine-tune the approach to make it amenable for use in process simulation software with multicomponent systems. Further work in this area would involve looking at the adsorption of mixtures--for example, the prediction and modeling of azeotropic adsorption. We would like to extend the ESD to modeling of zeolites. Also, more work needs to be done with hydrogen-bonding fluids such as water, as our efforts in applying the ESD in this particular area are not yet quantitative (Smith, 1997). Supercritical fluid adsorption is another subject of immediate interest since adsorption isotherms exhibit crossovers that can be represented with the SLD approach.

## **ACKNOWLEDGEMENTS**

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## **CHAPTER 4: CARBON DIOXIDE: A STUDY OF SUPERCRITICAL FLUID ADSORPTION**

Carbon dioxide is a fluid which has received much attention in adsorption studies as will be shown in this chapter. Chapter 2 is a typical example of its usefulness. Furthermore, the numerous methods of producing this gas make it cheap, and thus, favorable for use in chemical processes. A variety of experimental adsorption data is available in the literature, much of which at its supercritical conditions (above 304 K). Some of the different data will be examined and fitted with the SLD model in this chapter. The carbons presented here exhibit a wide range of surface areas depending on type: 983 to 1699 meters squared per gram. It can be seen that the fluid-solid interaction parameters vary widely with different carbons. They range from 77 K on DeGussa IV to 109 K on ACK carbon. The carbon dioxide Lennard-Jones diameter is 3.941 angstroms, taken from Reid, Prausnitz, and Poling. The fluid-solid interaction parameters and the slit width are optimized in each of these data sets.

Four different data samples have been fitted in this chapter at temperatures ranging from 212.7 K to 394.2 K. Figure 4-1 shows carbon dioxide adsorbed on DeGussa IV activated carbon at pressures up to 15 MPa. The isotherms at 284 K and 300 K exhibit adsorption maxima at 6.5 and 5 MPa respectively. The 324 K isotherm exhibits a maximum at 4 MPa; however, there is little data for analyzing its behavior beyond this point. Note that the peaks shown at the two higher temperatures were not fitted. Figure 4-2 shows carbon dioxide adsorption on Columbia Grade L carbon. The isotherms are more straight because the data set does not go significantly beyond the Henry's Law region. The optimized parameters give a good fit to this data, but these

same parameters might not give a good fit at higher pressures. The parameters are only valid for the pressure range in which they are fitted. Figure 4-3 shows a data set on BPL carbon which goes beyond the Henry's Law region at 260.2 K and 301.4 K, but not far enough to reach any maxima. Figure 4-4 shows a set which goes up to 15 MPa on ACK carbon. Note that, near 8 MPa, the isotherm at 313.2 K crosses over the isotherms at 333.2 K and 353.2 K. The 333.2 K and 353.2 K isotherms cross over one another at about 10.5 MPa. The SLD model agrees quite well with each of these crossover points in the data.

One special issue of concern in these fits is carbon surface area sensitivity. Each surface area is estimated with some margin of error. Changing the surface area does have an effect on the optimal parameters for a carbon-gas system. A quantitative analysis was performed on the ACK carbon system reported by Ozawa as shown in Table 4-1. The reported surface area (983 m<sup>2</sup>/g) was adjusted 10% in both the positive and negative directions. This test shows H and  $\epsilon_{fs}/k$  to increase with a decrease in surface area. Conversely, they both decrease with an increase in surface area. Note that  $\epsilon_{fs}/k$  changes by about the same amount in both the positive and negative directions while H tends to change most significantly with the decrease in surface area. Studies such as this should be considered depending upon the degree of uncertainty in a reported surface area.

**Table 4-1: Parameter Sensitivity to ACK Carbon Surface Area**

Area (m <sup>2</sup> /g)	H (angstroms)	$\epsilon_{fs}/k$ (K)
885	16.1	118
983	15.4	109
1081	15.2	99

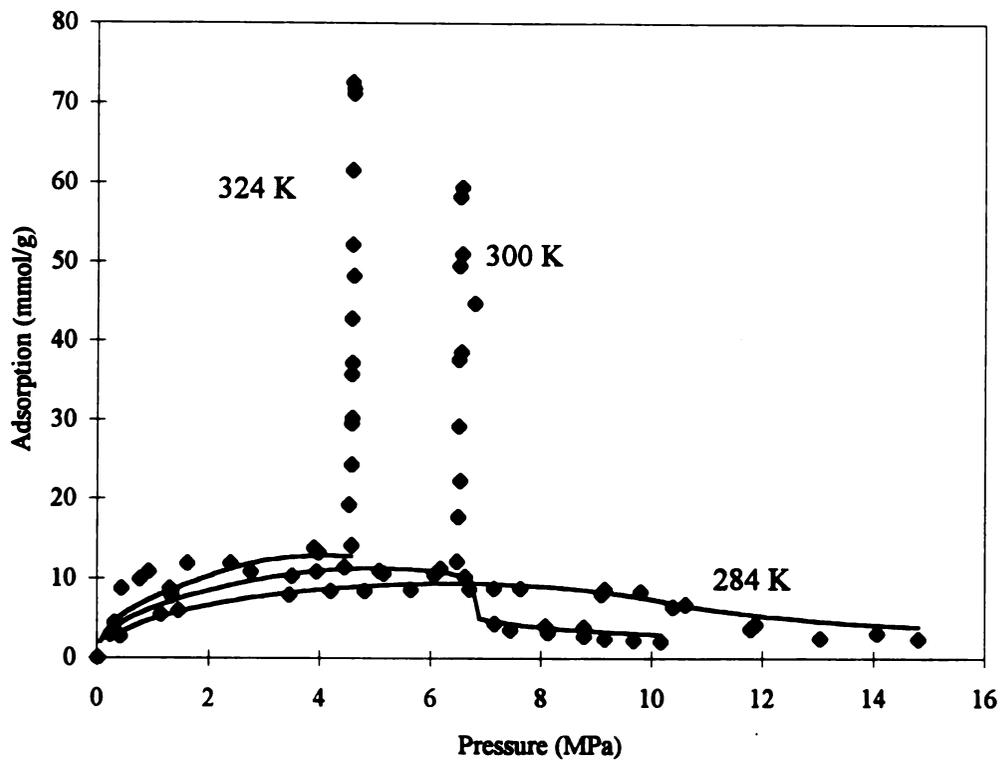


Figure 4-1: Carbon dioxide adsorption on DeGussa IV Activated Carbon (1699 meters squared per gram) where  $H=15.5 \text{ \AA}$  and  $\epsilon_p/k=77 \text{ K}$ . Data of Chen, et al., 1997.

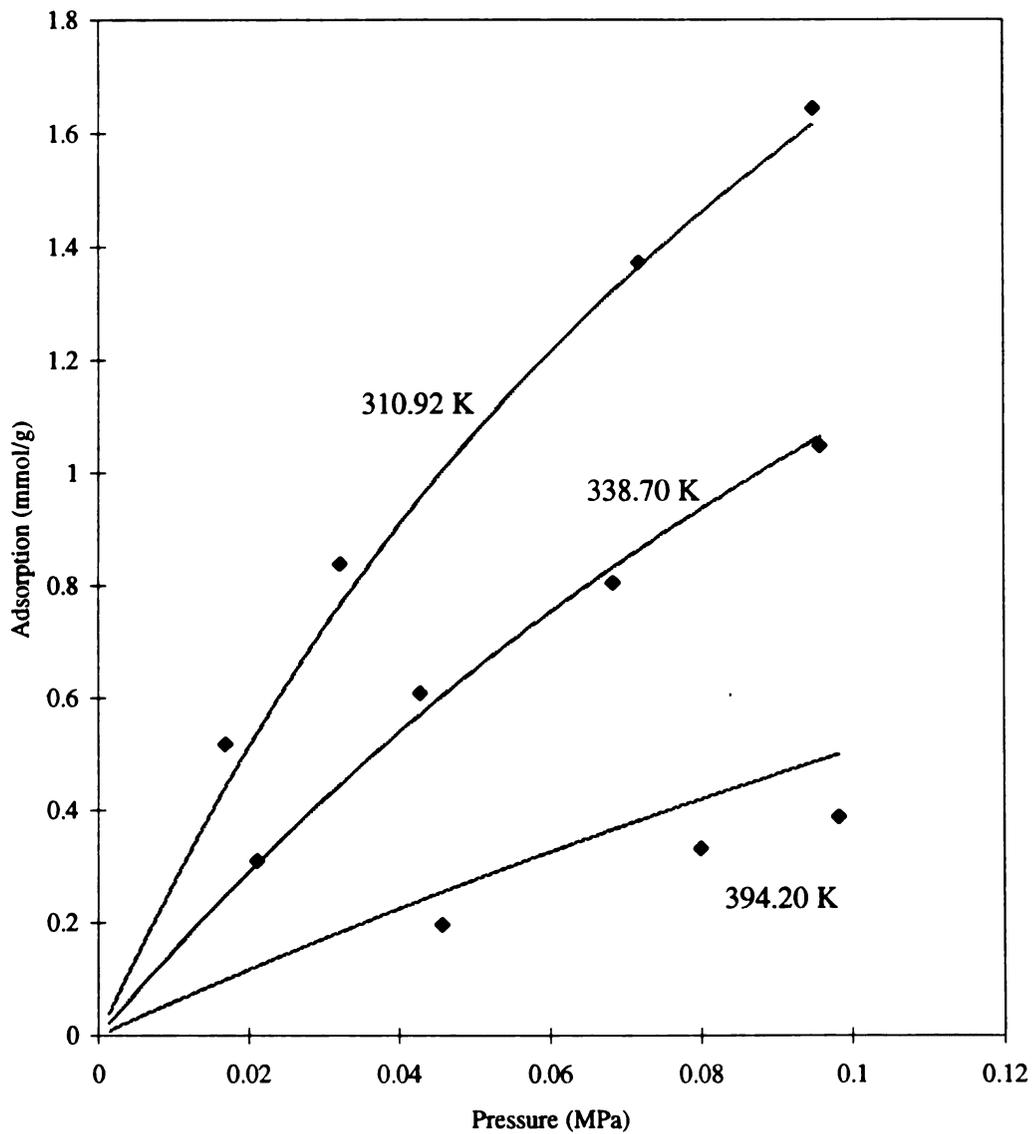


Figure 4-2: Carbon dioxide adsorption on Columbia Grade L Carbon (1152 meters squared per gram) where  $H=11.7$  A and  $\epsilon_f/k=86$  K. Data of Ray and Box, 1950.

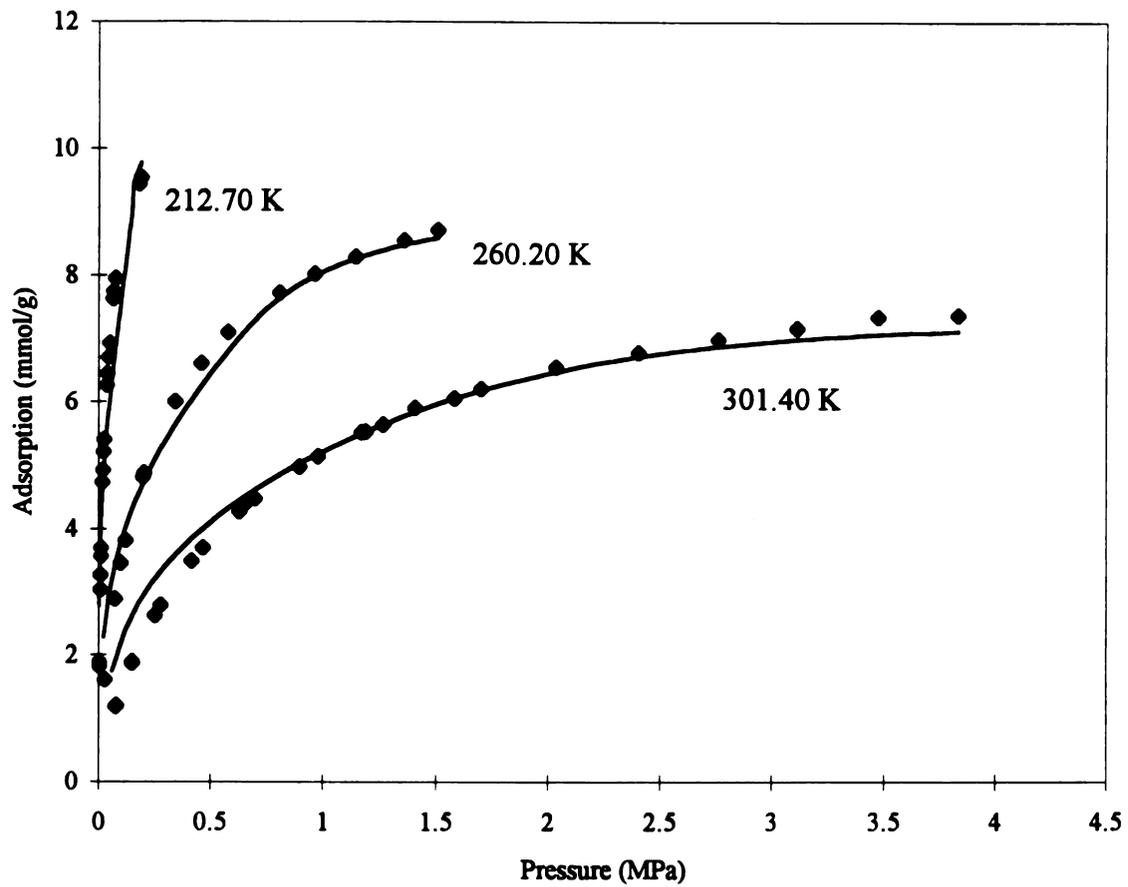


Figure 4-3: Carbon dioxide adsorption on BPL carbon (988 meters squared per gram) at  $H=14.2$  angstroms and  $\epsilon_B=99$  K. Data of Reich, et al., 1980.

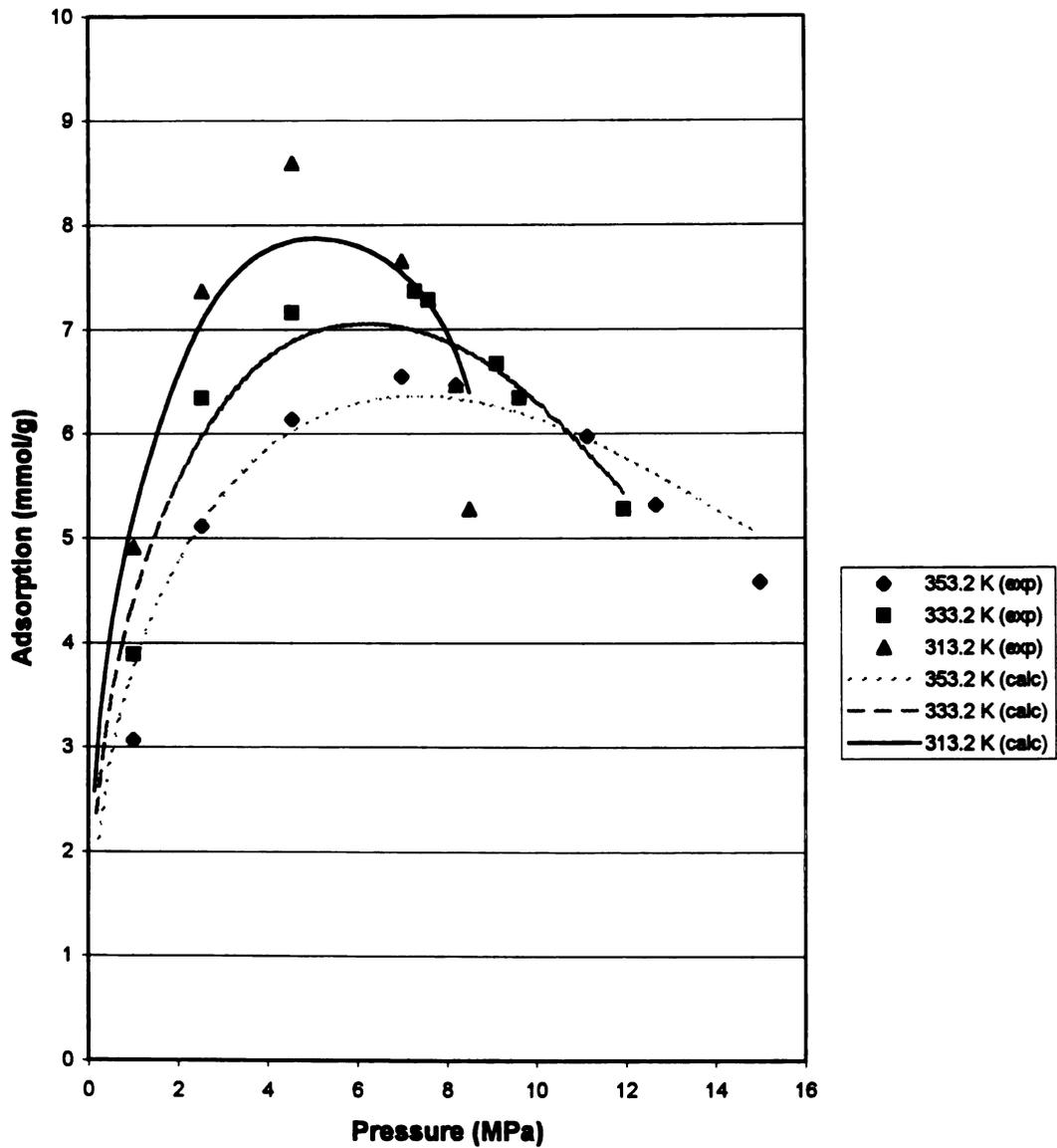


Figure 4-4: Adsorption of Carbon Dioxide on ACK Carbon (983 meters squared per gram) at  $H=15.4$  and  $\epsilon_{fg}/k=109$ . Data of Ozawa et al., 1974.

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## Chapter 5: ADSORPTION OF BINARY MIXTURES

### INTRODUCTION

In chapter 3, the SLD model was applied to adsorption of pure gases on activated carbon. This chapter attempts to extend that theory to mixtures modeled by the ESD equation of state. This particular work was started by Ramkumar Subramanian and was based on Peng-Robinson modeling. This current work takes the structure of his original FORTRAN program and converts it to one using ESD fluid properties. While the basic concepts do not change much from the modeling of pure fluids, there are mixing rules which must be obeyed in order to obtain correct fugacity values. This model uses three adjustable parameters as opposed to two for a pure system. The interactions of each component must be accounted for. Also, fugacity is solved for by satisfying a set of three objective functions at each local position.

### DISCUSSION

Elliott and Lira (1999) have developed all of the ESD mixing rules for binary systems along with a corresponding expression for the fugacity coefficient. In a binary system, each component is associated with a series of four tabulated ESD parameters:  $(e/k)_H$ ,  $c$  (dimensionless),  $q$  (dimensionless), and  $b$ . The expression for the fugacity coefficient of component A,  $\phi_A$ , is as follows. This equation assumes that no association occurs.

$$\ln(\phi_A) = T1 + T2 + T3 + T4 + T5 \quad (5-1)$$

where

$$T1 = -\frac{4}{19} c_A \ln(1 - 1.9\eta) \quad (5-2)$$

$$T2 = \frac{4cb_1\rho}{1 - 1.9\eta} \quad (5-3)$$

$$T3 = -\frac{9.5}{1.7745} \frac{\ln(1 + 1.7745 \langle Y\eta \rangle)}{\langle Yb \rangle} \left( \sum_{j=A}^B x_j Y_{Aj} (b_A q_j + b_j q_A) - \frac{\langle qYb \rangle}{\langle Yb \rangle} Y_A b_A \right) \quad (5-4)$$

$$T4 = -\frac{9.5 \langle qYb \rangle}{\langle Yb \rangle} \frac{Y_A b_A \rho}{1 + 1.7745 \langle Y\eta \rangle} \quad (5-5)$$

and

$$T5 = -\ln(Z) \quad (5-6)$$

The variables are defined as follows:  $\rho$  is density,  $Y$  is the ESD attractive parameter, and  $\eta = bp$ .  $Z$  is the compressibility solved from the cubic form of the ESD equation of state.

This cubic form is given as follows.

$$Z^3 + AA * Z^2 + BB * Z + CC = 0 \quad (5-7)$$

where

$$AA = 1.7745 * \langle Y * B \rangle - 1 - 1.9 * B \quad (5-8)$$

$$BB = -1.9 * 1.7745 * B * \langle Y * B \rangle - 1.7745 * \langle Y * B \rangle + 1.9 * B - 4 * c * B + 9.5 * \langle q * Y * B \rangle \quad (5-9)$$

and

$$CC = 1.9 * 1.7745 * B * \langle Y * B \rangle - 4 * 1.7745 * c * B * \langle Y * B \rangle - 9.5 * 1.9 * B * \langle q * Y * B \rangle \quad (5-10)$$

For the above equations,  $B = (b * P) / (R * T)$ .  $P$  is pressure,  $R$  is the ideal gas constant, and  $T$  is temperature. Furthermore, the following rules must be applied in calculating the mixture parameters from the pure component parameters. The variable  $x$  represents mole fraction.

$$b = \sum_{i=A}^B x_i b_i \quad (5-11)$$

$$c = \sum_{i=A}^B x_i c_i \quad (5-12)$$

$$q = \sum_{i=A}^B x_i q_i \quad (5-13)$$

$$Y_i = \exp(\varepsilon_i / kT) - 1.0617 \quad (5-14)$$

$$Y_{AB} = \exp(\varepsilon_{AB} / kT) - 1.0617 \quad (5-15)$$

$$\langle qY\eta \rangle = \rho \langle qYb \rangle = \rho \sum_{i=A}^B \sum_{j=A}^B x_i x_j Y_{ij} (b_i q_j + b_j q_i) / 2 \quad (5-16)$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} (1 - k_{AB}) \quad (5-17)$$

$$\langle Y\eta \rangle = \rho \langle Y^*b \rangle = \rho \sum_{i=A}^B x_i b_i Y_i \quad (5-18)$$

Note that equations 5-14 and 5-15 calculate Y values for the bulk phase only. In order to get Y values at a local position, expressions have been developed for  $Y/Y_{\text{bulk}}$  in a paper by Chen and coworkers (1997). In that paper, they are listed as  $a/a_{\text{bulk}}$  because the ratio expressions of the attractive parameter were originally derived using the Peng-Robinson equation. It is assumed that they also apply to the ESD equation of state.

Table 5-1 lists the parameters associated with the components under discussion in this manuscript along with their Lennard-Jones fluid diameters (Reid et al., 1987). Also, each mixture system has a mixture parameter,  $k_{ij}$ , which has been optimized for the best EOS fit to bulk data at a relevant temperature (Table 5-2). The data of Miller and coworkers (1977) were used for the methane-ethane and methane-ethylene systems. The data of Ng and Robinson (1978) were used for the toluene-carbon dioxide system. The toluene fluid-fluid diameter is set equal to that of benzene for this study (Reid et al., 1987) since no value is readily available in the literature.

**Table 5-1: Pure component fluid-fluid diameters and ESD parameters**

<b>Component</b>	$\sigma_{ff}$	$(\epsilon/k)_{ff}$ (K)	$b$ (cm <sup>3</sup> /mol)	$c$	$q$
<b>Carbon Dioxide</b>	3.941	178.269	10.534	1.8321	2.585
<b>Ethane</b>	4.443	220.429	16.716	1.3552	1.6765
<b>Ethylene</b>	4.163	210.275	15.013	1.305	1.581
<b>Methane</b>	3.758	178.082	10.863	1.0382	1.0728
<b>Toluene</b>	5.349	332.752	36.227	1.9707	2.849

One large assumption in this particular model is particle size homogeneity. Each mixture system uses an effective particle size,  $\sigma_{ij}$ , which is simply the average particle size of the two pure components. These values are also listed in Table 5-2. This assumption allows for the  $Y/Y_{bulk}$  values to be equivalent for each component. If the particle sizes were different, the  $Y/Y_{bulk}$  expressions for each component would be dependent on different definitions of the local position,  $\eta$  (in fluid-solid diameters). Also, separate exclusion regions for each component would have to be defined at the edges of the slit (regions where a particle is unable to realistically be present). At each end of the slit, these exclusion regions are equivalent to half of a fluid-solid diameter. Thus, separate particle sizes would require different regions of adsorption integration for each component. Since the work in this manuscript is of a preliminary nature, future work will involve formulating a more detailed mechanism for incorporating the individual particle size of each component.

In calculating wall-particle potentials, the diameter of the carbon itself is also important. This value,  $\sigma_{ss}$ , is 3.4 Angstroms (Subramanian, 1995). This gives rise to another important value, the fluid-solid diameter ( $\sigma_{fs}$ ), which is also tabulated in Table 5-2. This value is simply the average of the carbon diameter and the effective mixture fluid-fluid diameter.

Table 5-2: Mixing Parameters and Effective Mixture Diameters

Mixture	$\sigma_{ij}$	$\sigma_{fs}$	$k_{ij}$
Ethane-Methane	4.1	3.75	0.0094
Ethylene-Methane	4.0	3.70	0.0209
CO <sub>2</sub> -Toluene	4.6	4.00	0.1058

The algorithm for calculating adsorption is quite similar to that presented in Chapter 3. However, in this case, fugacity expressions are being matched for two different components (A and B) instead of just one at any local position or the bulk phase. Also, the  $Y/Y_{\text{bulk}}$  expressions cited in the paper by Chen and coworkers (as  $a/a_{\text{bulk}}$ ) must be used to solve for Y at each local position. These expressions are functions of local position and fluid particle size. As in Chapter 3, Eta represents the position in the slit in terms of fluid-solid diameters. The following equations define the 10-4 Lennard-Jones potentials relative to the first wall for each component:

$$\Psi_{1A}(z) = 4\pi\rho_{\text{atoms}}\sigma_{fs,A}^2\epsilon_{fs,A} \left\{ \begin{array}{l} \frac{0.2}{\text{Eta}^{10}} - \frac{0.5}{\text{Eta}^4} - \frac{0.5}{(\text{Eta} + \alpha)^4} \\ \frac{0.5}{(\text{Eta} + 2\alpha)^4} - \frac{0.5}{(\text{Eta} + 3\alpha)^4} - \frac{0.5}{(\text{Eta} + 4\alpha)^4} \end{array} \right\} \quad (5-18)$$

$$\Psi_{1B}(z) = 4\pi\rho_{\text{atoms}}\sigma_{fs,B}^2\epsilon_{fs,B} \left\{ \begin{array}{l} \frac{0.2}{\text{Eta}^{10}} - \frac{0.5}{\text{Eta}^4} - \frac{0.5}{(\text{Eta} + \alpha)^4} \\ \frac{0.5}{(\text{Eta} + 2\alpha)^4} - \frac{0.5}{(\text{Eta} + 3\alpha)^4} - \frac{0.5}{(\text{Eta} + 4\alpha)^4} \end{array} \right\} \quad (5-19)$$

The above two equations are identical due to the assumption of uniform particle diameter although each component will still maintain its fluid-solid interaction parameter ( $\epsilon_{fs}$ ).

Potentials relative to the second wall ( $\Psi_{2A}$  and  $\Psi_{2B}$ ) can be obtained by replacing Eta, the distance from the left wall to the local position, with Xi, the distance from the right wall to the local position of interest. Total potentials for each component can then be obtained from the following two equations:

$$\Psi_{TA} = \Psi_{1A} + \Psi_{2A} \quad (5-20)$$

$$\Psi_{TB} = \Psi_{1B} + \Psi_{2B} \quad (5-21)$$

Using these potentials, we can then proceed to define local fugacities relative to the bulk fugacities for each component as shown in the following equations:

$$f_{f,A}(z) = f_{bulk,A} \exp\left[\frac{-\Psi_{TA}(z)}{kT}\right] \quad (5-22)$$

$$f_{f,B}(z) = f_{bulk,B} \exp\left[\frac{-\Psi_{TB}(z)}{kT}\right] \quad (5-23)$$

Fugacity is also defined as the product of a fugacity coefficient ( $\phi$ ) and local pressure (P).

Thus, a series of three objective functions will now be introduced which can be solved for local composition ( $x_A$  and  $x_B$ ) and local pressure (P):

$$G1 = x_A * \phi_A * P / f_{ff,A} - 1 = 0 \quad (5-24)$$

$$G2 = x_B * \phi_B * P / f_{ff,B} - 1 = 0 \quad (5-25)$$

$$G3 = 1 - x_A - x_B = 0 \quad (5-26)$$

The fugacity coefficients are calculated by the ESD equation of state and are functions of composition and pressure. The coefficient expression and its pertinent mixing rules have been calculated by Elliott and Lira as shown in Equations 5-1 through 5-6. The following expressions define the integration necessary for producing adsorption values:

$$\Gamma_A^{EX} = A \int [x_A \rho(z) - x_{A,bulk} \rho_{bulk}] dz \quad (5-27)$$

$$\Gamma_B^{EX} = A \int [x_B \rho(z) - x_{B,bulk} \rho_{bulk}] dz \quad (5-28)$$

A is the surface area in meters squared per gram of activated carbon, z represents the local position in the slit, and  $\rho$  is density. The units of adsorption are millimoles adsorbed per gram of activated carbon.

## RESULTS

As previously noted, data sets for three different mixtures have been fitted using this theory. While the results are significantly better than those of Subramanian (1995), which incorporates the Peng-Robinson equation, there is still much room for improvement. Three adjustable parameters went into each fit: the fluid-solid interaction potentials for each component ( $(\epsilon_B/k)_A$  and  $(\epsilon_B/k)_B$  in Kelvin) and the carbon slit width (H in Angstroms). The component interaction potentials were all obtained from the pure data fits in chapter 3 with the exception of toluene. Due to a lack of literature data, the toluene fluid-fluid diameter is estimated to be 5.3 angstroms while its fluid-solid interaction potential is estimated to be 250 K. Since the ethylene-methane and ethane-methane data sets were obtained from the same carbon (BPL), an average slit width of 14 angstroms was used based on results from the pure systems in Chapter 3. As mentioned earlier, one weakness in the SLD theory is that different compounds do not always predict the exact same slit width for a single carbon.

While these parameters (except for toluene) have been optimized to pure component data, they have not been re-optimized to mixture data. This is a project which might be useful to pursue in the future; however, one aim of this particular work is to extrapolate pure component properties into mixture characterization. The values of the adjustable parameters are listed in Table 5-3. Note that there are different values for the

same component within different mixtures. This is due to the fact that the fluid-fluid potential for each component was fit using the effective particle diameter of the mixture rather than the tabulated diameter as in chapter 3.

**Table 5-3: Parameters Used In Mixture Calculations**

Component	$\sigma_{ij}$	$\epsilon/k$	H
<u>Methane-Ethane</u>			
Methane	4.1	66	14
Ethane	4.1	113	14
<u>Methane-Ethylene</u>			
Methane	4.0	68	14
Ethylene	4.0	108	14
<u>Toluene-CO<sub>2</sub></u>			
Toluene	4.6	250	20
CO <sub>2</sub>	4.6	73	20

Figures 5-1 through 5-7 contain methane-ethane fits at 301.4 K, 260.2 K, and 212.7 K on BPL carbon with a surface area of 988 m<sup>2</sup>/gram. Note that the methane adsorption is consistently under-predicted. However, the model seems to give an accurate fit for ethane in most cases. Ethane clearly is the more strongly adsorbed component. This behavior does not seem to change much over the 90 K temperature range. The homogeneous particle size assumption is likely to be a major cause of the error in methane prediction.

Figure 5-8 contains a methane-ethylene fit at 212.7 K on the same BPL carbon. Once again, methane is under-predicted, but the model fits well to ethylene. Consequently, the under-prediction of methane results in an over-prediction of ethylene's mole fraction in the adsorbed phase as shown in Figure 5-9.

Figure 5-10 shows toluene-CO<sub>2</sub> isotherms at 308 K, 318 K, and 328 K. With  $k_{ij}$  equal to 0.1058, it is clear that this is a non-ideal mixture. The SLD model (lines with

symbols) seems to consistently over-predict the data of Tan and Liou (lines without symbols). The predictions seem good at low pressures but then diverge at higher pressures. There seems to be some slope agreement between the data and the predicted values over the 20 K temperature range. Part of this error could be due to inaccuracies in the estimated toluene fluid-solid interaction parameter. Also, there is a comparatively large difference in the Lennard-Jones particle diameters. Carbon dioxide is 3.941 angstroms while toluene is estimated at 5.3 angstroms.

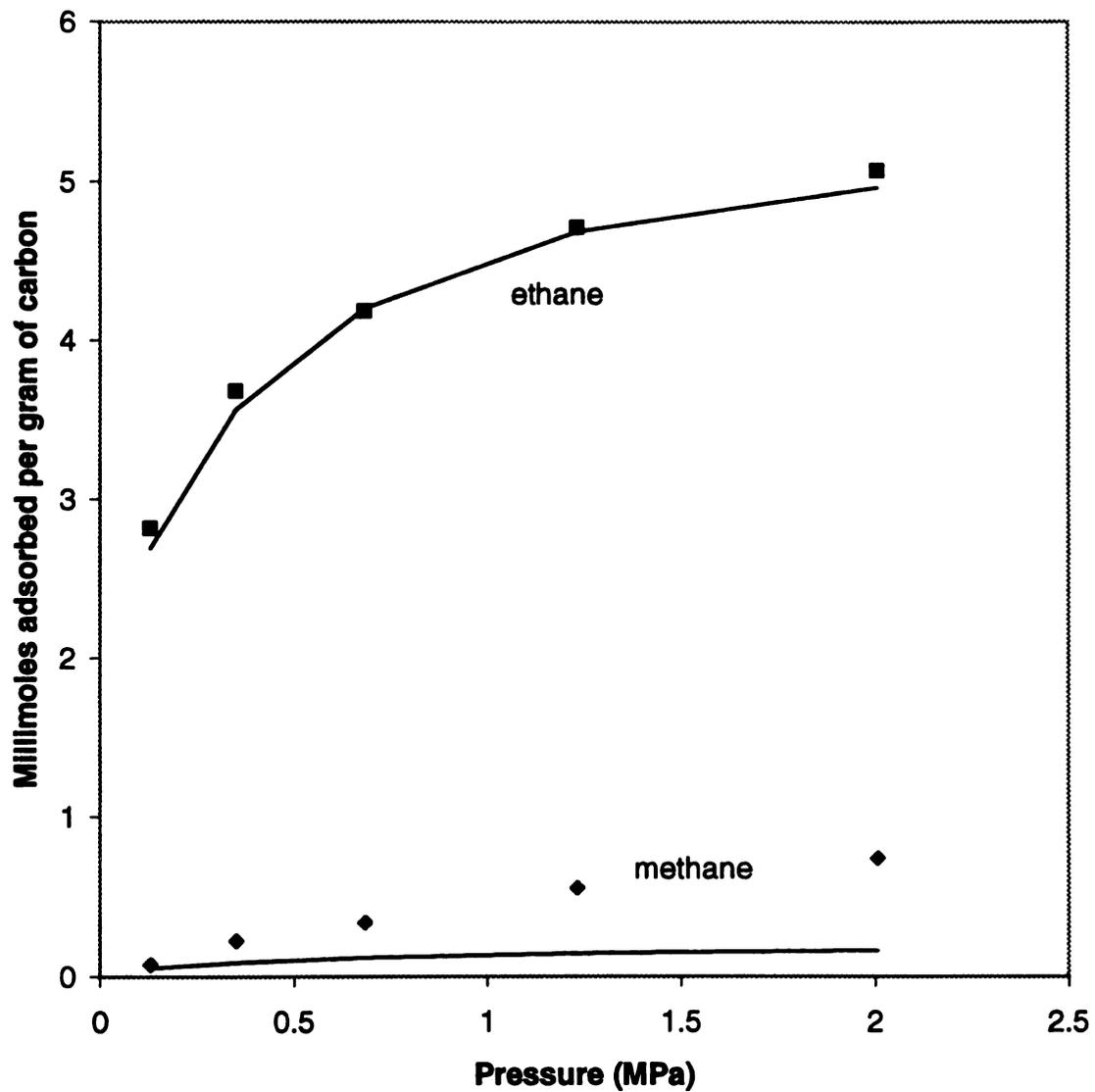


Figure 5-1: Adsorption of Methane-Ethane on BPL Activated Carbon at 301.4 K with Bulk Ethane Mole Fraction of 0.733 (Data of Reich, et al., 1980).

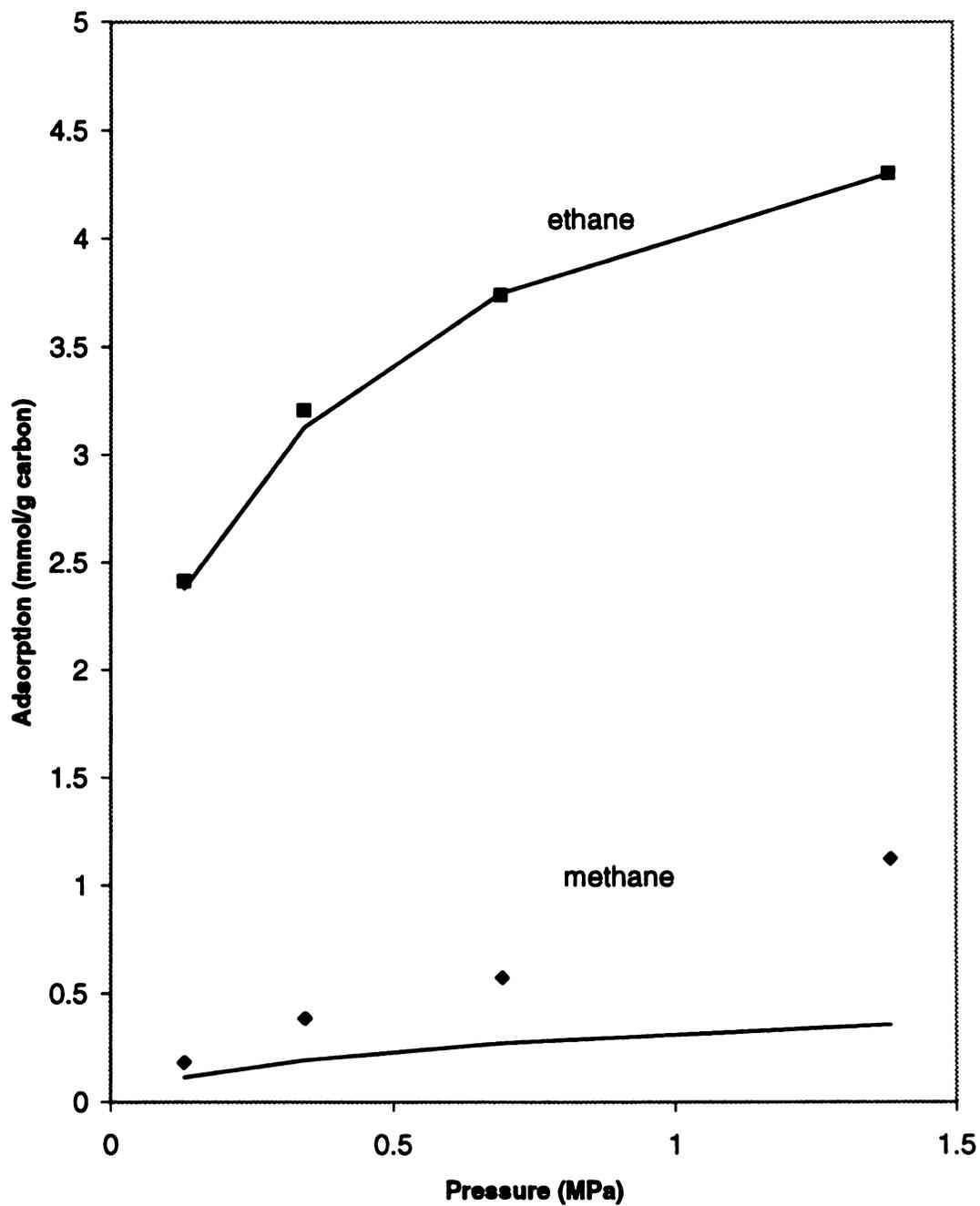


Figure 5-2: Adsorption of Methane-Ethane on BPL Carbon at 301.4 K and Bulk Ethane Fraction of 0.501 (Data of Reich, et al., 1980).

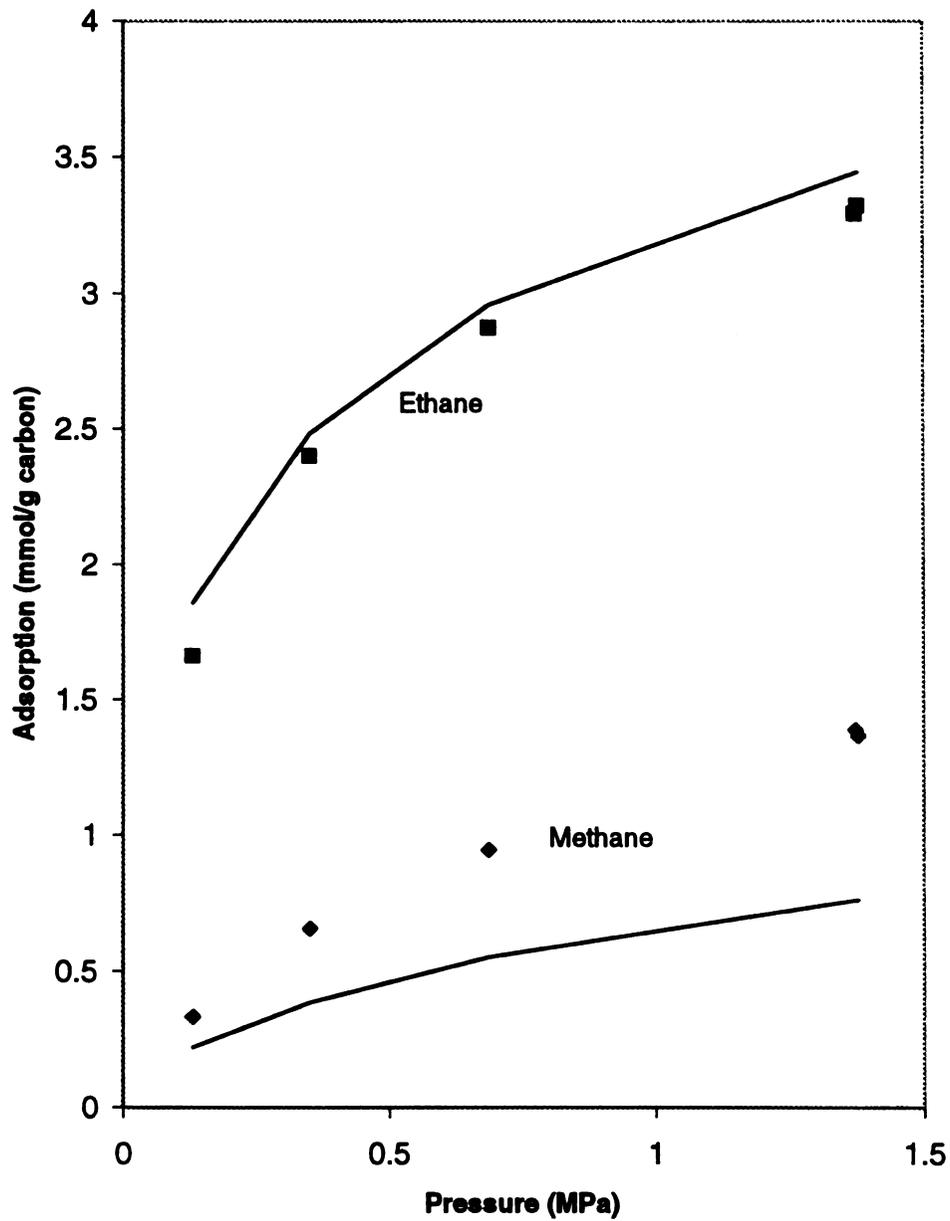


Figure 5-3: Adsorption of Methane-Ethane on BPL Carbon at 301.4 K and a Bulk Ethane Fraction of 0.255 (Data of Reich, et al., 1980).

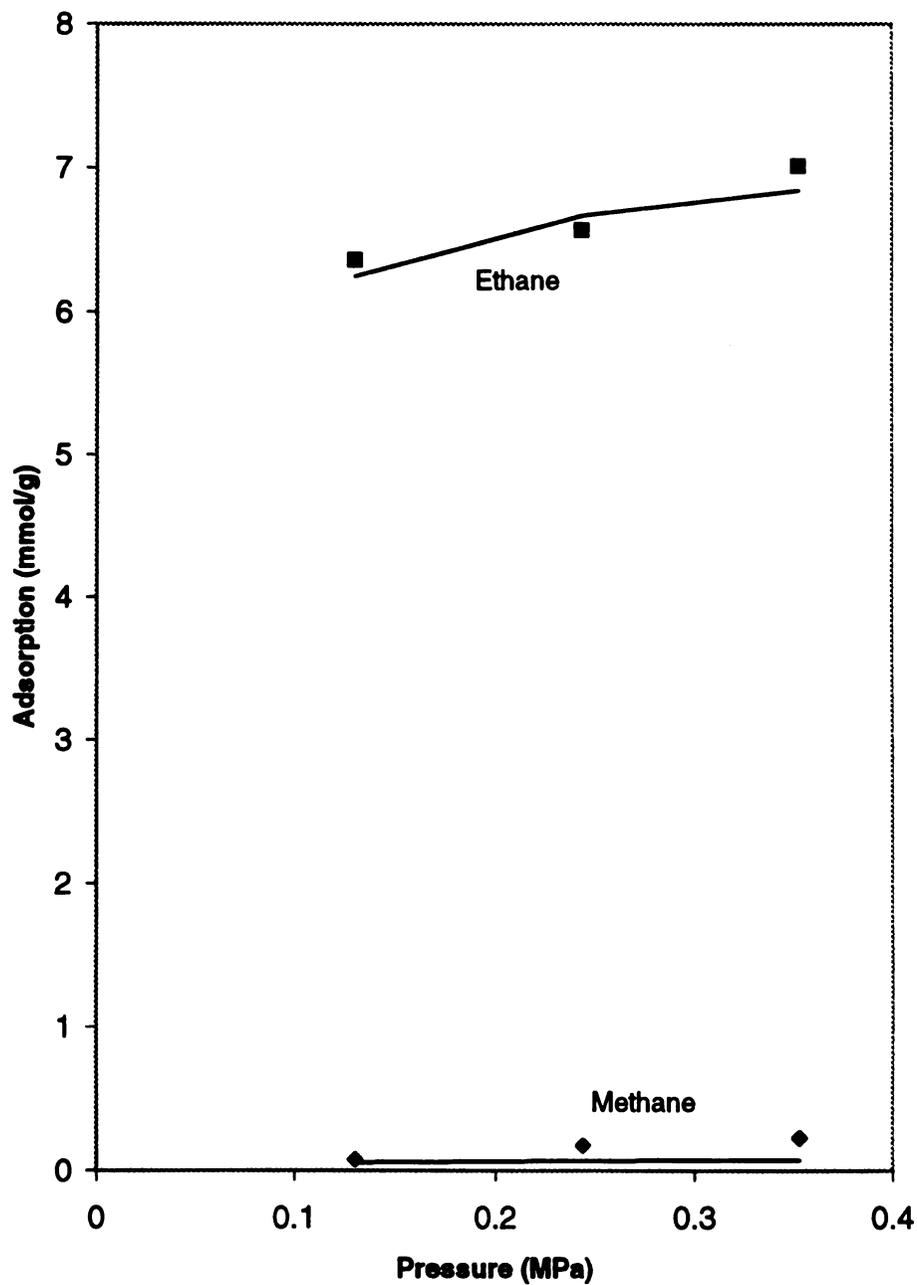


Figure 5-4: Adsorption of Methane-Ethane on BPL Carbon at 212.7 K and a Bulk Ethane Mole Fraction of 0.733 (Data of Reich, et al., 1980).

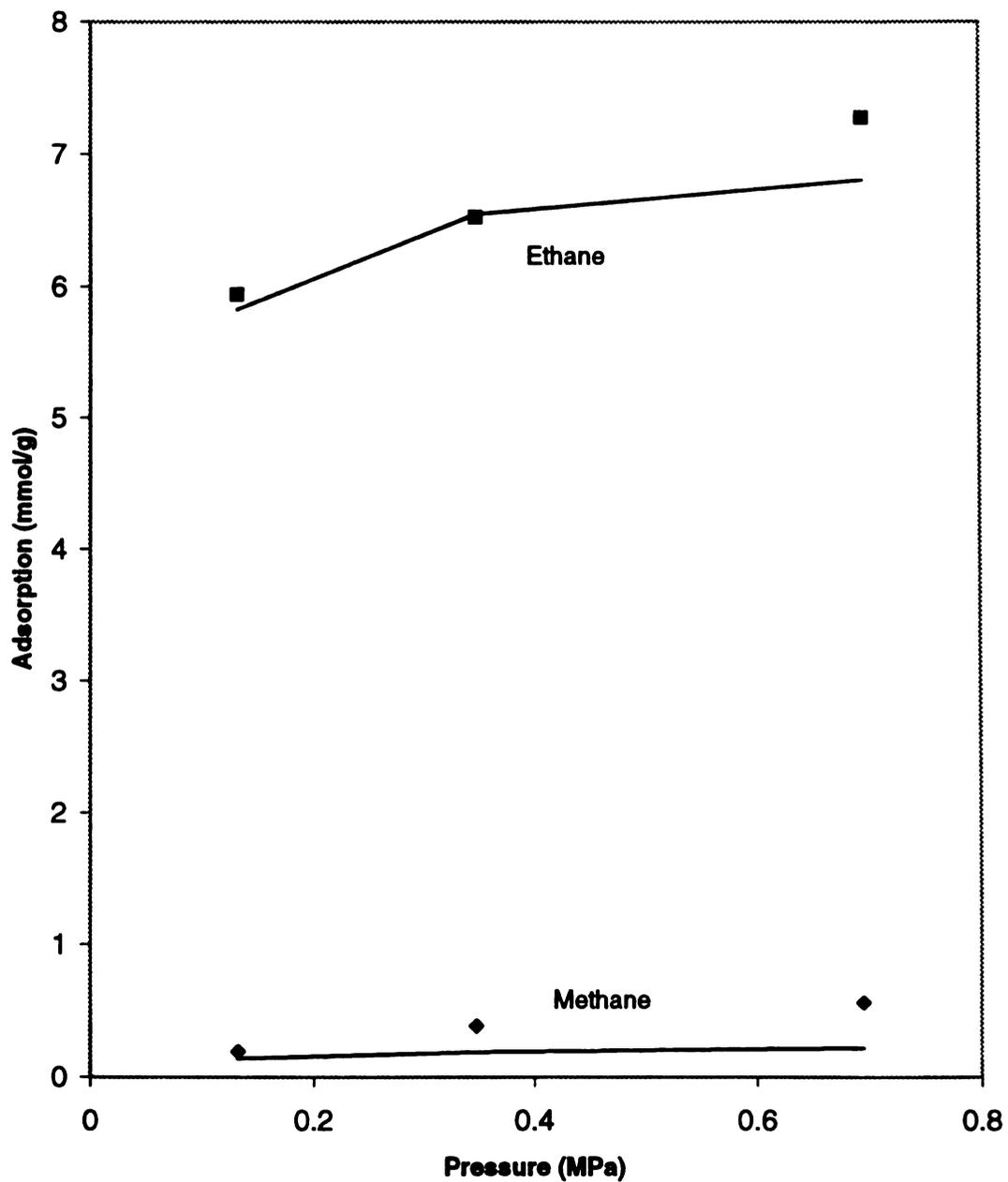


Figure 5-5: Adsorption of Methane-Ethane on BPL Carbon at 212.7 K and a Bulk Ethane Mole Fraction of 0.501 (Data of Reich, et al., 1980).

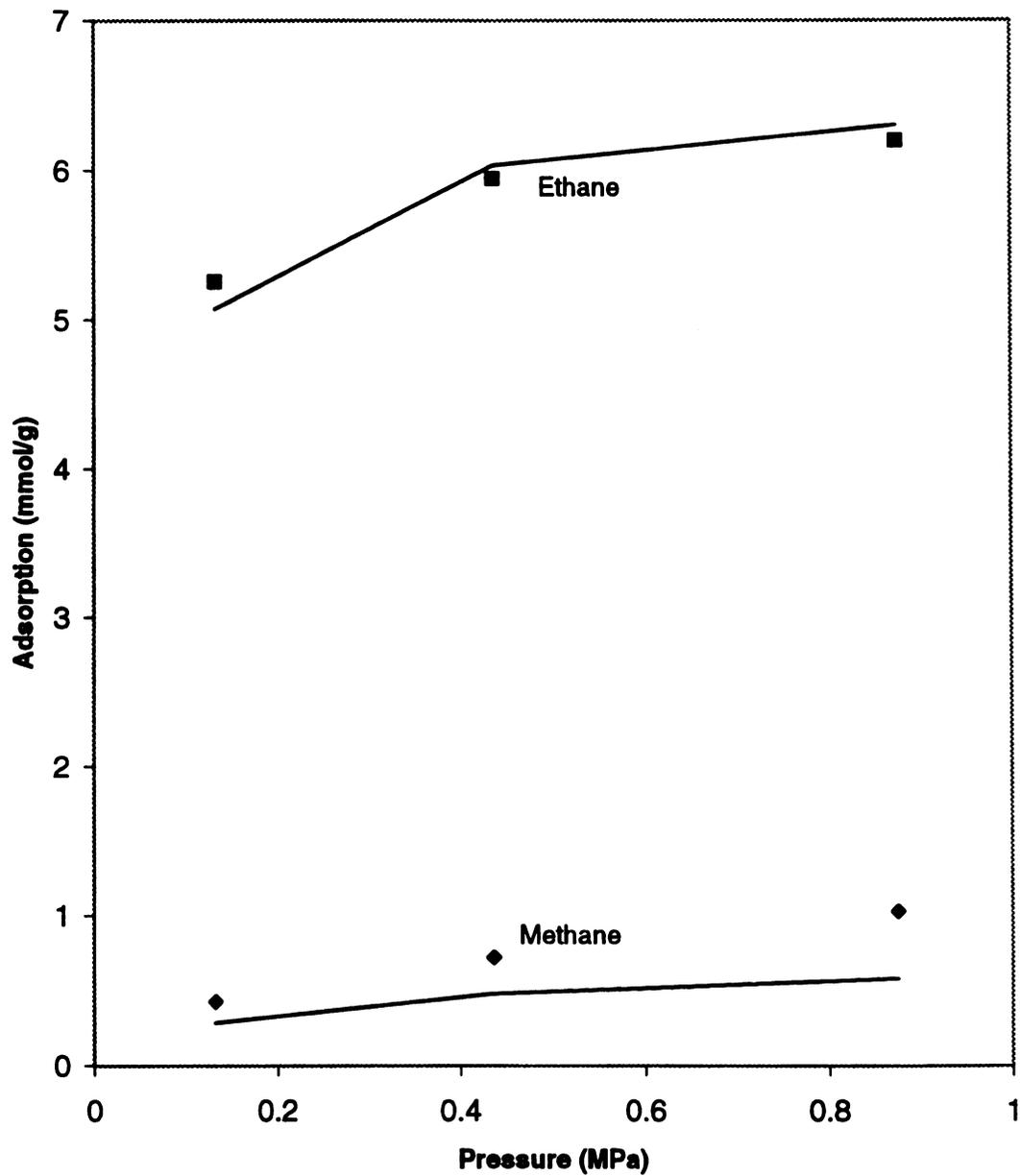


Figure 5-6: Adsorption of Methane-Ethane on BPL Carbon at 212.7 K and a Bulk Ethane Mole Fraction of 0.255 (Data of Reich, et al., 1980).

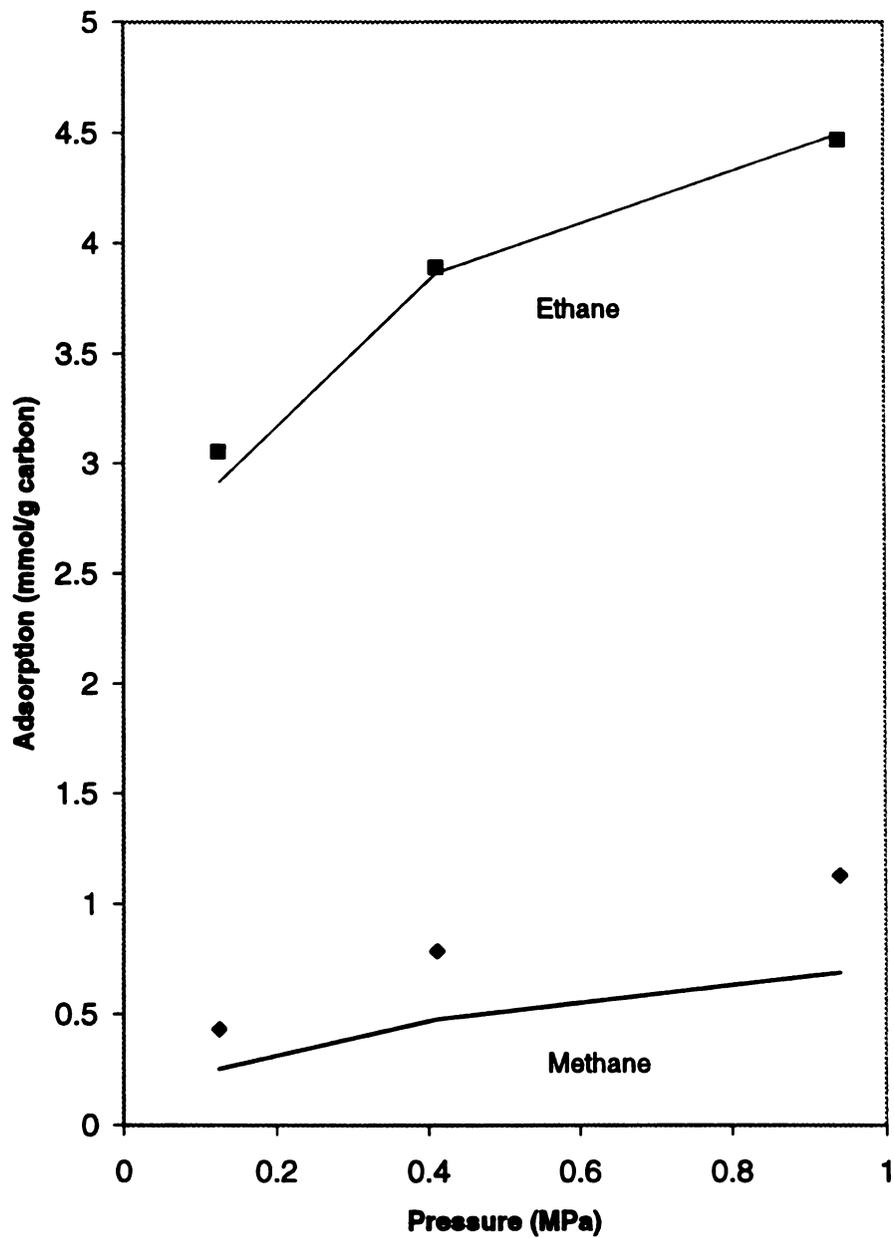


Figure 5-7: Adsorption of Methane-Ethane on BPL Carbon at 260.2 K and a Bulk Ethane Mole Fraction of 0.255 (Data of Reich, et al., 1980).

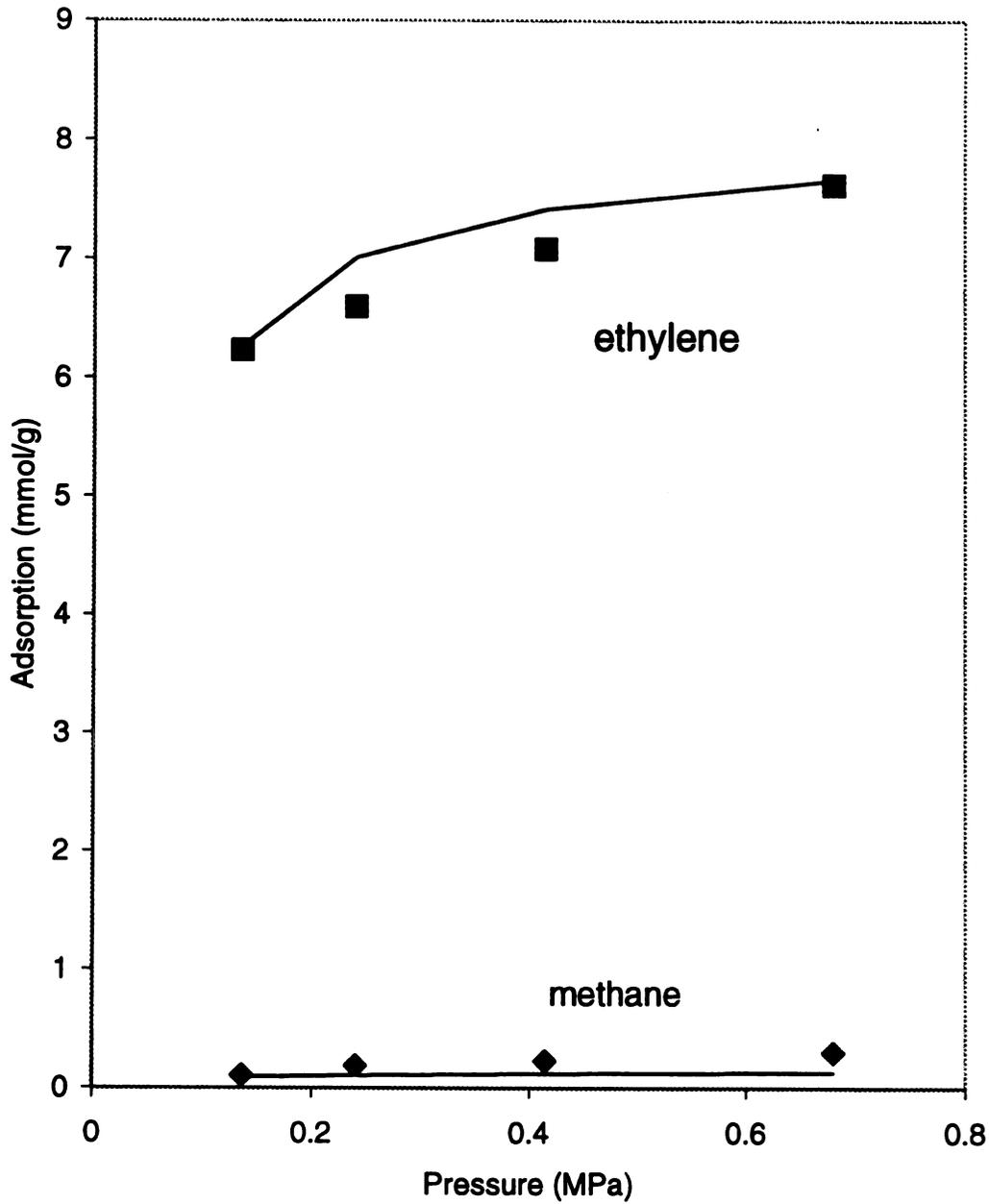


Figure 5-8: Methane-Ethylene Adsorption on BPL Carbon at 212.7 K and Initial Bul Ethylene Concentration of 0.74. Data of Reich, et al., 1980.

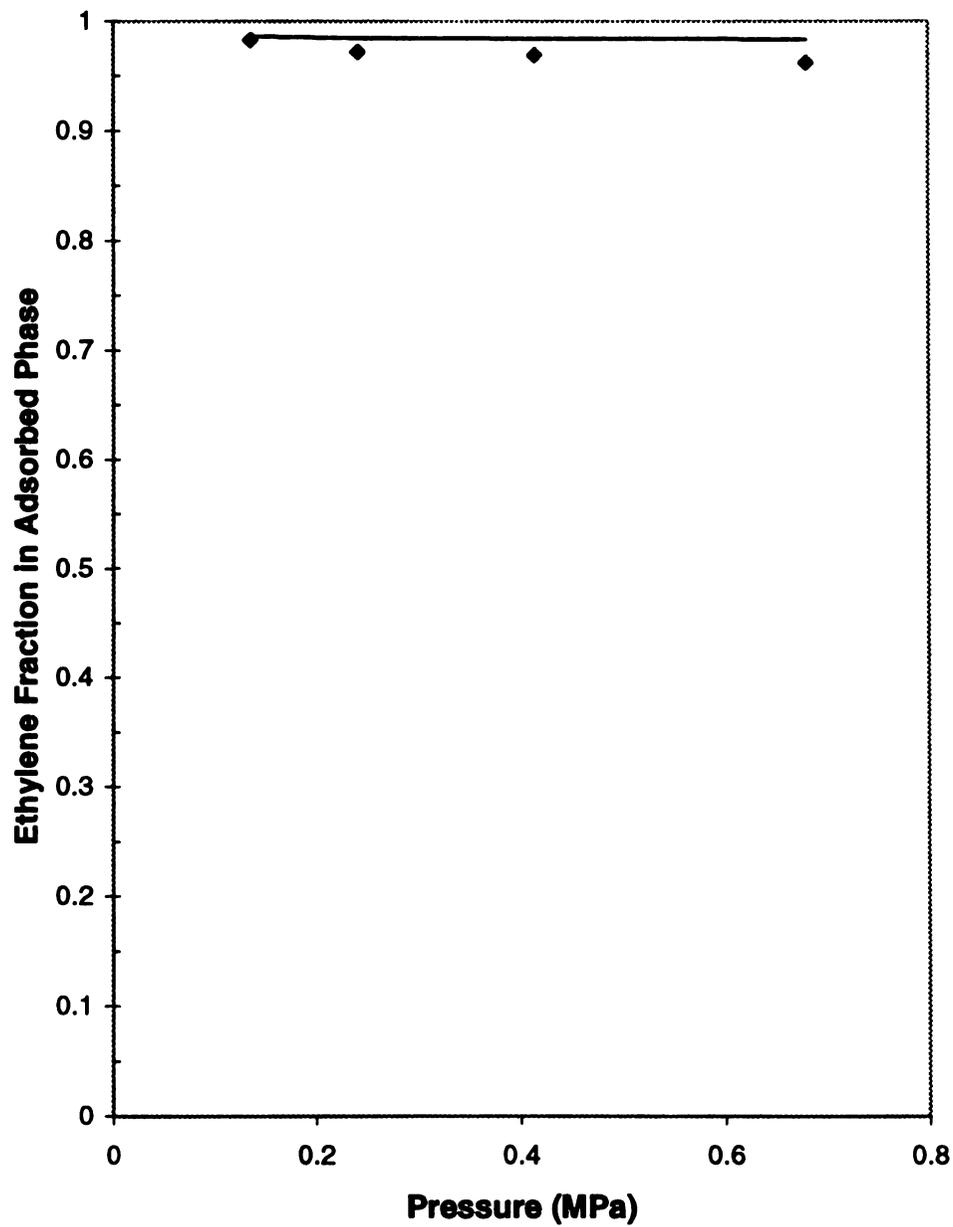


Figure 5-9: Adsorption of Ethylene-Methane Mixture on BPL carbon at 212.7 K and Initial Bulk Ethylene Concentration of 0.74 (Data of Reich, et al., 1980).

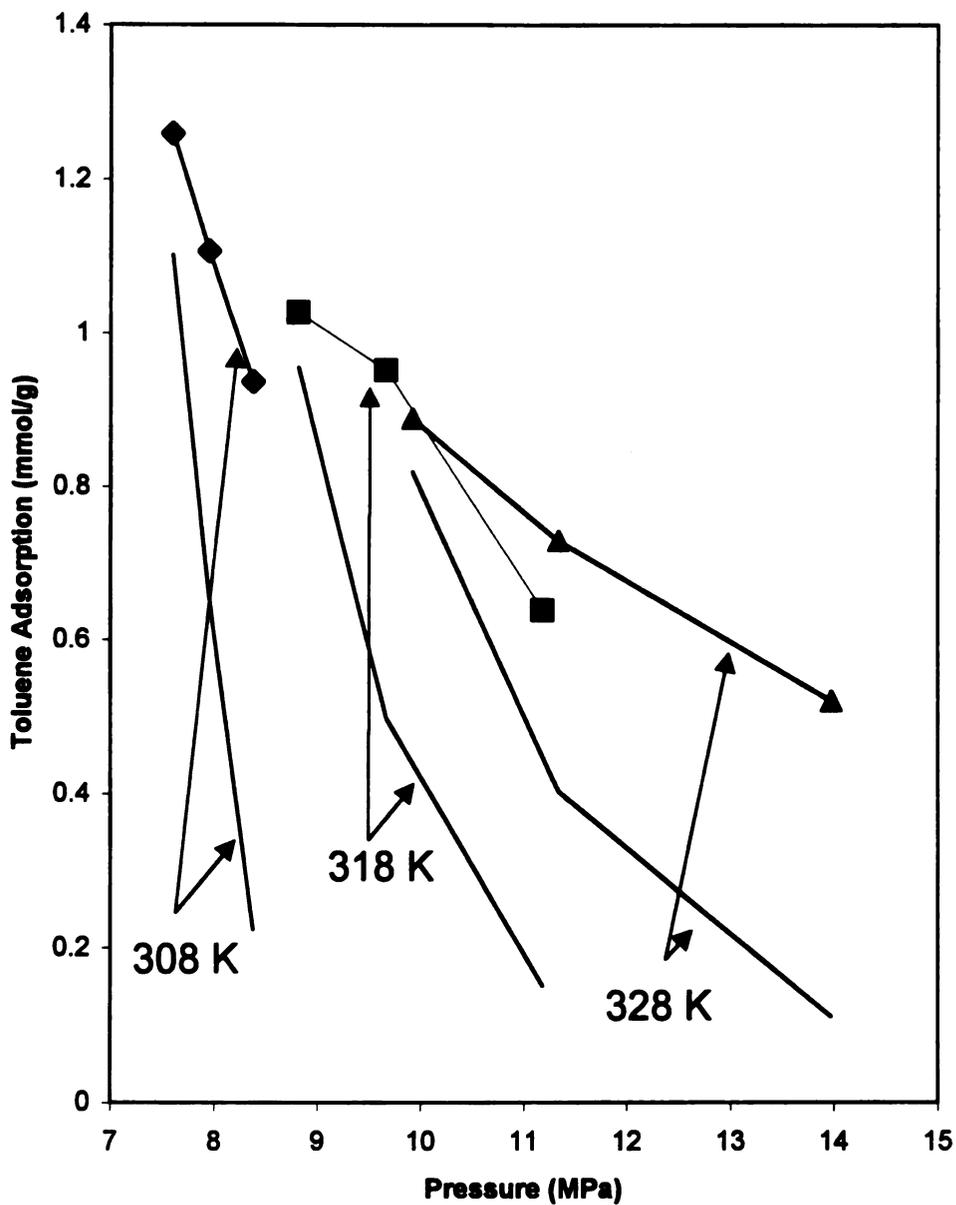


Figure 5-10: Pressure (density) effects of toluene adsorption on Degussa WSIV.  $C_{\text{toluene}} = 1 \text{ mmol/L}$  with data points at  $\rho_{\text{bulk}} = 6.3 \text{ mol/L}$ ,  $8.4 \text{ mol/L}$ , and  $10.8 \text{ mol/L}$  for each isotherm. Data of Tan and Liou, 1990.

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## **APPENDICES**

## **Appendix A: OPTIMIZING THE ADJUSTABLE PARAMETERS**

The SLITS program, as discussed in the master's thesis of Cassandra A. Smith, has two adjustable parameters,  $\epsilon_{fs}/k$  (fluid-solid interaction potential) and  $H$  (slit width). This thesis proposes a routine for optimally fitting these adjustable parameters to a data set. Before the advent of this OPTIMIZATION program, the adjustable parameters were fitted manually by trial and error. All of the fitted graphs in chapter 3 were generated from the OPTIMIZATION program in conjunction with the SLITS program. This chapter will discuss how the program was conceived and how it works.

### **INPUT**

In the user interface, the program asks for several pieces of information. It needs the ID number corresponding to the pure compound being analyzed. It also needs the surface area of the activated carbon on which the adsorption occurs. Approximate values for the two adjustable parameters also need to be supplied. An approximate value for  $\epsilon_{fs}/k$  can be estimated from the correlation shown in chapter 3.  $H$  is also not difficult to guess; based on all of the fits done,  $H$  usually falls between 12 and 16 angstroms. Also,  $H$  is a property of the carbon surface; it has no dependence (according to the SLD model) on the type of component being adsorbed. The program usually has no trouble optimizing these initial guesses. The user is also asked to select which of the two parameters to optimize first. This reasoning will be discussed in the next section.

A data file must also be supplied to the program. This data consists of the experimental isotherms. More than one isotherm can be entered and optimized at once. Basically, at a given temperature, there will be a list of pressures with the corresponding

molar adsorption per gram of carbon. The data file is formatted in such a way that the program will accept any number of data points and any number of isotherms. The only requirement is informing the program how many points/isotherms it needs to read in.

This is also built into the data file.

## **RATIONALE / METHOD**

The program reads in the pressures from the input file and runs them through a modified version of the SLITS program in order to generate a calculation for moles adsorbed. Once this is done for every data point, the modeled adsorption values are compared to the experimental adsorption values. A mean square error ( $\sum(\Gamma_{\text{exp}} - \Gamma_{\text{calc}})^2$ ) is then calculated. This is essentially the factor that determines how good the fit is.

The optimization is done one parameter at a time. The user chooses which one to optimize first. For example, if H is chosen,  $\epsilon_{\text{fb}}/k$  will be held constant while H is being adjusted to produce the minimum mean square error. First, H is coarsely adjusted by increments of 1 angstrom until the best value is found. Then H is more finely adjusted by increments of 0.1 angstrom until an optimal point is reached. One could choose to optimize at even smaller orders of magnitude, but those don't have much of an effect on the appearance of the fit. After H is successfully fitted, this new H value is held constant while  $\epsilon_{\text{fb}}/k$  is being adjusted to minimize the mean square error of the data.  $\epsilon_{\text{fb}}/k$  is first adjusted by increments of 10, then by increments of 1 and 0.1. After this is complete, the program determines whether the new parameter values are different from the initial guesses. If so, the procedure repeats itself until the fitted parameter values no longer change.

## **OUTPUT**

Once the optimal parameters are obtained, the user is given the option to plot a fitted curve to the data. For the fitted curve, the number of moles adsorbed is calculated for small increments of pressure up to the highest pressure given in each set of isotherm data. All of the experimental data and fitted data is then exported into an output file which can be easily imported into Excel and plotted.



! P is the optimization interval; Q determines whether E/k or H will  
! be optimized; R determines whether the parameters should be changed  
! in the positive or negative direction (1 pos., -1 neg.); T counts  
! how many times R changes during optimization, and thus, determines  
! when the parameters are optimized

```
WRITE(*,*) "Please prepare INDATA.DAT with your adsorption data,"  
WRITE(*,*) "or you can specify your input and output file names"  
WRITE(*,*) "within the code's OPEN statements."  
WRITE(*,*)  
WRITE(*,*) "Press 0 to quit or 1 to continue."  
READ(*,*) Response
```

```
IF (Response == 0) then  
  STOP  
ENDIF
```

```
WRITE(*,*) "Enter ID number of pure component."  
READ(*,*) ID
```

```
WRITE(*,*) "Enter the fluid particle diameter in angstroms."  
READ(*,*) SIGFF
```

```
WRITE(*,*) "Enter surface area of activated carbon."  
READ(*,*) AREA
```

```
5 FORMAT (F9.7, 5X, F8.4)
```

```
! *****  
! Section 2  
!  
! A generic data file will be read from; the data sets of interest  
! should be pasted into this file from different files  
! Read in experimental data  
! Each data set is assigned a temperature  
! Pressure (MPa) is in the first column; surface excess (mmol/g)  
! is in the second column  
! 2 arrays will be used to collect the pressure and excess data  
! *****
```

```
OPEN(UNIT=31, FILE='INDATA.DAT')
```

! The number of temperature profiles will be read in.

READ(31,\*) ENTRYNUMBER1

! Each set of adsorption data for the different temperatures  
! will now be read in.

DO COUNT1 = 1,ENTRYNUMBER1

READ(31,\*) ! Blank line

! The temperature of the specified set will be read in to  
! 2 decimal places

READ(31,\*) TEMP(COUNT1)

! The number of pressure/excess entries will now be read in

READ(31,\*) ENTRYNUMBER2(COUNT1)

! The individual pressure/excess entries will now be read in  
! Pressure--4 decimal places, in MPa  
! Surface Excess--4 decimal places, in mmol/g

READ(31,\*)

READ(31,\*)

DO COUNT2 = 1,ENTRYNUMBER2(COUNT1)

READ(31,\*) PRESSURE(COUNT1,COUNT2), EXCESS(COUNT1,COUNT2)

END DO

READ(31,\*)

END DO

! \*\*\*\*\*  
! Section 3  
!  
! User will provide guess values for H and E/k (EPSOVERK)  
! A modified version of the Slit program is called to calculate  
! surface excess at the pressures specified by the above data  
! file--> the calculated surface excess values will be stored  
! in a third array  
! \*\*\*\*\*

```

WRITE(*,*) "TEMP(1)=",TEMP(1)
WRITE(*,*) "PRESSURE(1,1)=",PRESSURE(1,1)
WRITE(*,*) "PRESSURE(2,1)=",PRESSURE(2,1)
WRITE(*,*) "ENTRYNUMBER1=",ENTRYNUMBER1
WRITE(*,*) "ENTRYNUMBER2=",ENTRYNUMBER2

WRITE(*,*) "Enter guess values for H and E/k respectively."
READ(*,*) H, EPSOVERK
WRITE(*,*) "Which parameter do you wish to optimize first?"
WRITE(*,*) "E/k (0) or H (1)? "
READ(*,*) Q

IF (Q == 1) THEN
  P = 1
ELSE
  P = 10
ENDIF

H2 = H
EPSOVERK2 = EPSOVERK
MEMORY = 1

100 IF (MEMORY > 190) THEN
  MEMORY = 1      ! resets array after most of the spaces are full
ENDIF

  ERRORCOUNT = 0
  H3(MEMORY) = H
  EPSOVERK3(MEMORY) = EPSOVERK

  IF (MEMORY > 1) THEN
    DO ARCHIVE = 1,(MEMORY - 1)
      IF (H == H3(ARCHIVE) .AND. EPSOVERK == EPSOVERK3(ARCHIVE))
THEN
        ERRORCOUNT = ERRORARRAY(ARCHIVE)
      ENDIF
    END DO
  ENDIF

  IF (ERRORCOUNT == 0) THEN

    DO COUNT1 = 1,ENTRYNUMBER1

    DO COUNT2 = 1,ENTRYNUMBER2(COUNT1)
      X1 = TEMP(COUNT1)
      X2 = PRESSURE(COUNT1,COUNT2)

```

```
CALL MODIFIEDSLIT(X1,X2,H,EPSOEVERK,X3,ID,AREA,SIGFF)
  EXCESSCA(COUNT1,COUNT2) = X3
```

```
  ERROR = (EXCESSCA(COUNT1,COUNT2) -
EXCESS(COUNT1,COUNT2))**2
  ERRORCOUNT = ERRORCOUNT + ERROR
END DO
END DO
```

```
ENDIF
```

```
ERRORARRAY(MEMORY) = ERRORCOUNT
```

```
MEMORY = MEMORY + 1
```

```
! *****
! Section 4
!
! The experimental surface excess values will be compared to the
! calculated surface excess values, and thus, a value representing
! error will be calculated (ERRORCOMP).
!
! LOOP 4A
! A loop will be set up to adjust E/k at constant H in order to
! minimize ERRORNEW. The guess value of E/k will either be
! increased or decreased by increments of 10, 1, and .1 respectively
! until error is minimized. The new set of parameters will be
! provided to the modified slit program described in section 3.
!
! LOOP 4B
! A loop will be set up to adjust H at constant E/k for the
! minimization of ERRORNEW. The guess value of H will either be
! increased or decreased by increments of 1 and .1 until error is
! minimized. The new set of parameters will be provided to the
! modified slit program described in section 3 for each case.
!
! LOOP 4C
! The two parameters will be adjusted as many times as necessary by
! the two loops described above until a minimum error value is
! converged upon.
!
```

! \*\*\*\*\*

ERRORNEW = ERRORCOUNT

! B is a marker cataloging the error change as a function of the  
! parameter changes

IF (ERRORNEW > ERROROLD) THEN

  B=0

ENDIF

IF (ERRORNEW < ERROROLD) THEN

  B=1

ENDIF

IF (T > 1) THEN

  B=2

ENDIF

150 IF (Q == 0) THEN

! Minimization of E/k at constant H

  WRITE(\*,\*) "Optimizing E/k"

    WRITE(\*,\*) "ERRORNEW=",ERRORNEW

    WRITE(\*,\*) "EPSOVERK=",EPSOVERK

    WRITE(\*,\*) "H=",H

    WRITE(\*,\*) "B=",B

    WRITE(\*,\*) "EXCESSCA(1,1)=",EXCESSCA(1,1)

200 IF (B == 1) THEN

  WRITE(\*,\*) "Adjusting E/k"

  IF (R == 1) THEN

    EPSOVERK = EPSOVERK + P

  ENDIF

  IF (R == -1) THEN

    EPSOVERK = EPSOVERK - P

  ENDIF

  ERROROLD = ERRORNEW

  GOTO 100

ENDIF

IF (B == 0) THEN

  WRITE(\*,\*) "Changing direction for E/k"

```
R=-R
B=1
T=T+1
GOTO 200
```

```
ENDIF
```

```
IF (B == 2) THEN
  WRITE(*,*) "Changing E/k increment"
  P=P/10
  B=1
  T=0
  IF (P < 1) THEN
    WRITE(*,*) "E/k optimization completed"
    P=1
    Q=1
    GOTO 150
  ENDIF
  GOTO 200
```

```
ENDIF
```

```
ENDIF
```

```
IF (Q == 1) THEN
```

```
! Minimization of H at constant E/k
  WRITE(*,*) "Optimizing H"
  WRITE(*,*) "ERRORNEW=",ERRORNEW
  WRITE(*,*) "EPSOVERK=",EPSOVERK
  WRITE(*,*) "H=",H
  WRITE(*,*) "B=",B
  WRITE(*,*) "EXCESSCA(1,1)=",EXCESSCA(1,1)
```

```
600 IF (B == 1) THEN
```

```
  WRITE(*,*) "Adjusting H"
  IF (R == 1) THEN
    H = H + P
  ENDIF
  IF (R == -1) THEN
    H = H - P
  ENDIF
```

```
  ERROROLD = ERRORNEW
  GOTO 100
```

```

    ENDIF
IF (B == 0) THEN
    WRITE(*,*) "Changing direction for H"
    R=-R
    B=1
    T=T+1
    GOTO 600

ENDIF

IF (B == 2) THEN
    WRITE(*,*) "Changing H increment"
    P=P/10
    WRITE(*,*) "P = ",P
    B=1
    T=0
    IF (P < 0.09) THEN
        WRITE(*,*) "H optimization complete"
        P=10
        Q=0
        GOTO 1000
    ENDIF
    GOTO 600

```

```
ENDIF
```

```
ENDIF
```

! The difference in the last two values for each parameter will  
! now be tabulated as a fraction of their current values

```
1000 CHANGE1 = ABS(H2 - H)/H
```

```
CHANGE2 = ABS(EPSOVERK2 - EPSOVERK)/EPSOVERK
```

```
WRITE(*,*) "CHANGE1=",CHANGE1
WRITE(*,*) "CHANGE2=",CHANGE2
```

```
IF (CHANGE1 < 0.001 .AND. CHANGE2 < 0.001) THEN
    GOTO 1510
ENDIF
```

```
H2 = H
EPSOVERK2 = EPSOVERK
```

GOTO 200

```
! *****  
! Section 5  
!  
! The experimental and fitted data points will now be plotted  
! side-by-side on the same output file.  
!  
! *****
```

1500 FORMAT(A,F6.2)

1510 WRITE(\*,\*)

WRITE(\*,1500) " EPSOVERK = ",EPSOVERK

WRITE(\*,1500) " H = ",H

WRITE(\*,\*)

1600 Response = 1

WRITE(\*,\*) "Generate complete fitted curve with data? (Y=1/N=2)"

READ(\*,\*) Response

IF (Response == 2) THEN

OPEN(UNIT=32, FILE='OUTDATA.DAT',STATUS='REPLACE')

2000 WRITE(32,\*) "Isotherm Output"

WRITE(32,\*)

WRITE(32,\*) "The first column is pressure in MPa."

WRITE(32,\*) "The second column is experimental adsorption (mmol/g)."

WRITE(32,\*) "The third column is fitted adsorption (mmol/g)."

WRITE(32,\*) "Each section of data is preceded by temperature (K)."

2010 FORMAT(A,F8.2,A)

WRITE(32,2010) "Adsorbent surface area is ",AREA, &  
" square meters per gram."

2020 FORMAT(A,F6.2)

WRITE(32,2020) " EPSOVERK = ",EPSOVERK

WRITE(32,2020) " H = ",H

WRITE(32,\*)

WRITE(32,\*)

2100 FORMAT(10X,F10.6,6X,F10.4,6X,F10.4)

```

DO COUNT1 = 1,ENTRYNUMBER1

WRITE(32,*)
WRITE(32,'(F6.2)') TEMP(COUNT1)
WRITE(32,*)
DO COUNT2 = 1,ENTRYNUMBER2(COUNT1)
X1 = PRESSURE(COUNT1,COUNT2)
X2 = EXCESS(COUNT1,COUNT2)
X3 = EXCESSCA(COUNT1,COUNT2)
WRITE(32,2100) X1,X2,X3
END DO

END DO

CLOSE (32)

ELSE

OPEN(UNIT=33, FILE='OUTDATA2.DAT',STATUS='REPLACE')

WRITE(*,*)
WRITE(*,*) "Curve is being generated in OUTDATA2.DAT"
WRITE(*,*)
WRITE(33,*) "Isotherm Output"
WRITE(33,*)
WRITE(33,*) "The first column is pressure in MPa."
WRITE(33,*) "The second column is experimental adsorption (mmol/g)."
WRITE(33,*) "The third column is fitted adsorption (mmol/g)."
WRITE(33,*) "Each section of data is preceded by temperature (K)."
2210 FORMAT(A,F8.2,A)
WRITE(33,2210) "Adsorbent surface area is ",AREA, &
" square meters per gram."
2220 FORMAT(A,F6.2)
WRITE(33,2220) " EPSOVERK = ",EPSOVERK
WRITE(33,2220) " H = ",H
WRITE(33,*)
WRITE(33,*)

2230 FORMAT(10X,F10.6,22X,F10.4)
2240 FORMAT(10X,F10.6,6X,F10.4)

DO COUNT1 = 1,ENTRYNUMBER1

WRITE(33,*)
WRITE(33,'(F6.2)') TEMP(COUNT1)
WRITE(33,*)

```

```

X1 = TEMP(COUNT1)
X2 = PRESSURE(COUNT1,ENTRYNUMBER2(COUNT1))

CALL
SLITCURVES(X1,X2,H,EPSOVERK,ID,AREA,PRESSUREFIT,ADSORP,LMNO,SIG
FF)

DO L=1,LMNO          ! LMNO is the number of pressure increments
                    ! used to plot the curve
WRITE(33,2230) PRESSUREFIT(L),ADSORP(L)
END DO

DO COUNT2 = 1,ENTRYNUMBER2(COUNT1)
WRITE(33,2240) PRESSURE(COUNT1,COUNT2),
EXCESS(COUNT1,COUNT2)
END DO

END DO

CLOSE(33)

ENDIF

CLOSE (31)

Response = 1
WRITE(*,*)
WRITE(*,*) "Fit is complete."
WRITE(*,*)
WRITE(*,*) "Do you wish to fit another data set (Y=1/N=2)?"
READ(*,*) Response

IF (Response == 1) THEN
GOTO 1
ENDIF

! CLOSE(60)

5000 END

```

## Modified SLITS

SUBROUTINE MODIFIEDSLIT(T,BLKP,H,EPSFS,AMTS,ID,AREA,SIGFF)

```
! *****
!     TEMP: Temperature in Kelvin
!     PRESSURE: Pressure in MPa
!     H: Slit width in angstroms
!     EPSFS: Fluid-solid attractive parameter
!
! *****
```

```
!     THIS PROGRAM CALCULATES EXCESS IN A SLIT FOR MIXTURES
USING
!     THE ESD EQUATION OF STATE. A SQUARE WELL POTENTIAL HAS
BEEN ADDED.
```

```
!     Z IS FROM CARBON SURFACE. THEREFORE, ZOSFF=0 AT THE
SURFACE OF WALL.
```

```
!     ZLCL IS DISTANCE FROM CARBON CENTER IN FLUID-SOLID
DIAMETERS.
```

```
!     ZLCL IS EQUIVALENT TO ETA IN PREVIOUSLY WRITTEN PROGRAMS.
```

```
IMPLICIT DOUBLE PRECISION(A-H,K,O-Z)
```

```
DOUBLE PRECISION, INTENT(IN) :: T,BLKP,H,EPSFS,AREA
```

```
INTEGER, INTENT(IN) :: ID
```

```
DOUBLE PRECISION, INTENT(OUT) :: AMTS
```

```
CHARACTER*1 ANSWER
```

```
CHARACTER*2 KIND
```

```
CHARACTER*20 NAME
```

```
PARAMETER (NMX=10)
```

```
DIMENSION
```

```
TC(NMX),PC(NMX),ACEN(NMX),ZFEED(NMX),S(NMX),NAME(NMX)
```

```
COMMON/ESD/KCSTAR(NMX),DH(NMX),C(NMX),Q(NMX),VX(NMX),
```

```
COMMON/ESD/VLK(NMX),ND(NMX),EOKP(NMX)
```

```
COMMON/ETA/ETAL,ETAV,ZL,ZV
```

```
COMMON/EQN/KIND, APPX
```

```
COMMON/CONSTK/KIJ(NMX,NMX),INITIAL
```

```
COMMON/FEED/ZFEED
```

```
COMMON/KVALUES/S
```

```
COMMON/NAME/NAME
```

```
COMMON/LOCAL/DELTAZ
```

```
COMMON FKEEP
```

```
DIMENSION LCLDENS(200),FUGBULK(NMX),PSI(NMX),FUGLCL(NMX)
```

```
DIMENSION FUG(NMX),FUGCCALC(NMX),XA(NMX),FKEEP(NMX)
```

```
COMMON/POSITION/ZLCL
DOUBLE PRECISION LCLDENS,EXCE,LOSFF,RHOD,FKEEP
DOUBLE PRECISION FUG,RHO,PB,SIGFF,FUGLCL,ZOSFF,SIGFS,SIGSS
! COMMON/INTERACTIONS/SIGFF, SIGFS,SIGSS
DIMENSION X(NMX),IER(12),Y(NMX),PSI1(NMX),PSI2(NMX),RHOD(200)
```

```
1 NC = 1
  INITIAL=0
```

```
1100 CALL GETCRIT(NC,ID,NAME,TC,PC,ACEN)
```

```
  IF(ID.EQ.0)GO TO 1100
```

```
  CALL GETESD(NC,ID,EOKP,KCSTAR,DH,C,Q,VX,ND)
```

```
  DO 15 I=2,NC
```

```
    DO 10 J=1,I-1
```

```
      CALL ESTACT(ID,I,J,EOKP,VX,KIJ)
```

```
10  CONTINUE
```

```
15  CONTINUE
```

```
30  CONTINUE
```

```
  MAXIT=11111
```

```
  ! LOCAL PRESSURE AUTOMATICALLY INITIALIZED FROM BULK
  PRESSURE
```

```
  ANSWER=1
```

```
  INIT=0
```

```
1000 CONTINUE
```

```
  RGAS=8.31434
```

```
!
```

```
! X=1 IS THE BULK COMPOSITION (PURE COMPONENT)
```

```
!
```

```
X(1) = 1
```

```
! SQUARE WELL POTENTIAL DISABLED
```

```

WELLP = 0
WELLD = 0

EXCE=0
AMTS=0
ADSORB=0

!   SIGFF=0.
!   DO 12 I=1,NC
!       CALL SIGMAFIND(ID,I,SIGMA,NC)

!   SIGFF=(SIGMA(I)+SIGFF)

12   CONTINUE

      SIGSS=3.4
      SIGFS=0.5*(SIGFF+SIGSS)
      ALPHASP=3.35/SIGFS

LMNO=65.
      DELP=BLKP/LMNO
      PB=0
      IFLAG=0
      ZLCL=0

      FACTOR=0.1

      J=1
      LOSFF=(H-SIGSS)/SIGFF

!3   Pressure increment loop deleted
      PB=BLKP           ! CHANGED TO BULK PRESSURE
71   BULK=1
      LIQ=0
      FSQD=0.
      CALL FUGI(TC,RGAS,T,PB,X,NC,LIQ,FUGCCALC,ZVB,IER,RHOB,BULK,
&
      XA,FSQ,ALPHA,FSQD,LOSFF,ZOSFF)

      DO 29 I=1,NC
29   FKEEP(I)=FUGCCALC(I)
      ZKEEP=ZVB
      RHOKEEP=RHOB
      LIQ=1

```

```

&
CALL FUGI(TC, RGAS, T, PB, X, NC, LIQ, FUGCCALC, ZVB, IER, RHOB, BULK,
&
      XA, FSQ, ALPHA, FSQD, LOSFF, ZOSFF)

DO 203 I=1, NC
IF(FUGCCALC(I).GT.FKEEP(I))THEN
FUGCCALC(I)=FKEEP(I)
ZVB=ZKEEP
RHOB=RHOKEEP
ENDIF
203 CONTINUE

PLCL=PB

DO 17 I=1, NC
17 FUGBULK(I)=X(I)*PB*FUGCCALC(I)

! LAST MUST BE AN ODD NUMBER. IT IS THE NUMBER OF POINTS
GENERATED.
LAST=199.

EXCE=0
AMTS=0
ADSORB=0

DELTAZ=(LOSFF-2.*FACTOR)/(LAST-1)
ZOSFF=FACTOR-DELTAZ

DO 77 ISTEP=1, LAST
5 ZOSFF=ZOSFF+DELTAZ
ZLCL=(ZOSFF*SIGFF+0.5*SIGSS)/SIGFS
XI=(LOSFF*SIGFF+SIGSS/2.-ZOSFF*SIGFF)/SIGFS

ITMAX=MAXIT
DO 32 I=1, NC
PSI1(I)=4.0*3.1415926*0.382*SIGFS*SIGFS*EPSFS*(-0.2 &
/ZLCL**10+0.5/ZLCL**4+0.5/(ZLCL+ALPHASP)**4+0.5/(ZLCL+2.0* &
ALPHASP)**4+0.5/(ZLCL+3.0*ALPHASP)**4+0.5/(ZLCL+4.0*ALPHASP) &
**4)

PSI2(I)=4.0*3.1415926*0.382*SIGFS*SIGFS*EPSFS*(-0.2 &
/XI**10+0.5/XI**4+0.5/(XI+ALPHASP)**4+0.5/(XI+2.0* &
ALPHASP)**4+0.5/(XI+3.0*ALPHASP)**4+0.5/(XI+4.0*ALPHASP) &
**4)

```

PSI(I)=PSI1(I)+PSI2(I)

SQWL=0.

DIST1=(ZLCL-SIGSS/SIGFS/2.)\*SIGFS

DIST2=(XI-SIGSS/SIGFS/2.)\*SIGFS

! SQUARE WELL POTENTIAL FOR A SINGLE COMPONENT ONLY

IF(DIST1.LE.(WELLD\*SIGFF))SQWL=WELLP

IF(DIST2.LE.(WELLD\*SIGFF))SQWL=WELLP

FUGLCL(I)=FUGBULK(I)\*DEXP((PSI(I)+SQWL)/T)

32 CONTINUE ! LN(f)=mu

IF(J.EQ.1)THEN

DO 50 I=1,NC

IF(PSI(I).LT.-2500.)THEN

p=0

GOTO 5

ELSE

p=p+1

endif

50 CONTINUE

if(p.eq.1)then

FACTOR=ZOSFF

DELTAZ=(LOSFF-2\*FACTOR)/(LAST-1)

p=p+1

ENDIF

ENDIF

J=2

! WRITE(60,\*) 'ISTEP = ',ISTEP,' in MODIFIEDSLIT'

! WRITE(60,\*) 'PLCL = ',PLCL,' in MODIFIEDSLIT'

! WRITE(60,\*) 'BLKP = ',BLKP,' in MODIFIEDSLIT'

CALL

BUBPL(TC,RGAS,T,NC,Y,IER,PLCL,FUG,RHO,XA,FUGLCL,LOSFF,ZOSFF)

6 continue

DO 11 I=1,12

11 IF (IER(I).NE.0)IFLAG=1

IF (IFLAG.EQ.1)WRITE(6,\*)'IER',(IER(I),I=1,6)

IF(IER(2).EQ.1)WRITE(\*,\*)'ERROR ALL VAPOR'

```

IF(IER(3).EQ.1)WRITE(*,*)'ERROR ALL LIQUID'
IF(IER(4).EQ.4)WRITE(*,*)'ERROR IN FUGI-NEG LOG CALCD'
IF(IER(4).EQ.5)WRITE(*,*)'ERROR IN FUGI-FUGACITY OVERFLOWS'
IF(IER(5).EQ.1)WRITE(*,*)'ERROR VAPOR AND LIQUID ROOTS CLOSE'
IF(IER(6).EQ.1)WRITE(*,*)'ERROR VLE ITERATION NO CNVRG,ITMAX'
IF(IER(7).EQ.1)WRITE(*,*)'ERROR VLE ITERATION FAILED TO IMPROVE'
IF(IER(8).EQ.1)WRITE(*,*)'ERROR IN TC,PC,OR X,Y'
IF(IER(9).EQ.1)WRITE(*,*)'ERROR P SPECIFIED < 0'
IF(IER(10).EQ.1)WRITE(*,*)'ERROR T SPECIFIED IS UNREASONABLE'
IF(IER(11).EQ.1)WRITE(*,*)'ERROR MORE THAN 10 COMPONENTS'
  IF(IFLAG.EQ.1)PAUSE
  IF(IFLAG.EQ.1)STOP

!      LCLDENS IN MOL/CM3
44     LCLDENS(ISTEP)=RHO-RHOB
       RHOD(ISTEP)=RHO

       IF(ISTEP.EQ.(LAST))THEN
         DO 99 I=1,(LAST-2),2
           POSIT1=I
           POSIT2=I+1
           POSIT3=I+2
!       EXCESS IN MICROMOLES/M^2
EXCE=SIGFS*DELTAZ*10**2*(LCLDENS(POSIT1)+4.*LCLDENS(POSIT2)+
&
  LCLDENS(POSIT3))/6.+EXCE

ADSORB=SIGFS*DELTAZ*10**2*(RHOD(POSIT1)+4.*RHOD(POSIT2)+
&
  RHOD(POSIT3))/6.+ADSORB
!     AMT DIVIDED BY 2 IN SLIT INTEGRATIONS
99    CONTINUE
!     AREA IN M^2/G, AMT IN MMOL/G
AMTS = EXCE*AREA/1000.
ENDIF

77    CONTINUE

!End of original pressure increment loop

82    CONTINUE

```

! NOTE: FOR REPEAT BP CALCULATIONS IT IS ASSUMED THAT  
BOOTSTRAPPING  
! IS DESIRED. OTHERWISE, THE USER SHOULD ANSWER 'N' TO  
! THE REPEAT QUESTION BELOW AND GO BACK THROUGH THE MAIN  
! PROGRAM BEFORE PROCEEDING.

! THIS REPEAT STATEMENT HAS BEEN CHANGED TO START THE  
PROGRAM  
! OVER. THE ABOVE NOTE IS INVALID.  
! INIT=1

END

## SLITS Curve Generation

SUBROUTINE

SLITCURVES(T,BLKP,H,EPSFS,ID,AREA,PRESSURE,ADSORP,LMNO,SIGFF)

! THIS PROGRAM GENERATES A FITTED PRESSURE CURVE FOR THE  
OUTPUT

! FILE

! \*\*\*\*\*

!       TEMP: Temperature in Kelvin  
!       PRESSURE: Pressure in MPa  
!       H: Slit width in angstroms  
!       EPSFS: Fluid-solid attractive parameter

! \*\*\*\*\*

!       THIS PROGRAM CALCULATES EXCESS IN A SLIT FOR MIXTURES  
USING  
!       THE ESD EQUATION OF STATE. A SQUARE WELL POTENTIAL HAS  
BEEN ADDED.

!       Z IS FROM CARBON SURFACE. THEREFORE, ZOSFF=0 AT THE  
SURFACE OF WALL.

!       ZLCL IS DISTANCE FROM CARBON CENTER IN FLUID-SOLID  
DIAMETERS.

!       ZLCL IS EQUIVALENT TO ETA IN PREVIOUSLY WRITTEN PROGRAMS.

IMPLICIT DOUBLE PRECISION(A-H,K,O-Z)

DOUBLE PRECISION, INTENT(IN) :: T,BLKP,H,EPSFS,AREA

INTEGER,INTENT(IN) ::ID

DOUBLE PRECISION AMTS

DOUBLE PRECISION, INTENT(OUT) :: PRESSURE(100),ADSORP(100)

INTEGER, INTENT(OUT) :: LMNO

CHARACTER\*1 ANSWER

CHARACTER\*2 KIND

CHARACTER\*20 NAME

PARAMETER (NMX=10)

DIMENSION

TC(NMX),PC(NMX),ACEN(NMX),ZFEED(NMX),S(NMX),NAME(NMX)

COMMON/ESD/KCSTAR(NMX),DH(NMX),C(NMX),Q(NMX),VX(NMX),

COMMON/ESD/VLK(NMX),ND(NMX),EOKP(NMX)

```

COMMON/ETA/ETAL,ETAV,ZL,ZV
COMMON/EQN/KIND,APPX
COMMON/CONSTK/KIJ(NMX,NMX),INITIAL
COMMON/FEED/ZFEED
COMMON/KVALUES/S
COMMON/NAME/NAME
COMMON/LOCAL/DELTAZ
COMMON FKEEP
DIMENSION LCLDENS(200),FUGBULK(NMX),PSI(NMX),FUGLCL(NMX)
DIMENSION FUG(NMX),FUGCCALC(NMX),XA(NMX),FKEEP(NMX)
COMMON/POSITION/ZLCL
DOUBLE PRECISION LCLDENS,EXCE,LOSFF,RHOD,FKEEP
DOUBLE PRECISION FUG,RHO,PB,SIGFF,FUGLCL,ZOSFF,SIGFS,SIGSS
! COMMON/INTERACTIONS/SIGFF, SIGFS,SIGSS
DIMENSION X(NMX),IER(12),Y(NMX),PSI1(NMX),PSI2(NMX),RHOD(200)

OPEN(UNIT=55,FILE='OUTDATA.DAT')

1 NC = 1
INITIAL=0

1100 CALL GETCRIT(NC,ID,NAME,TC,PC,ACEN)

IF(ID.EQ.0)GO TO 1100

CALL GETESD(NC,ID,EOKP,KCSTAR,DH,C,Q,VX,ND)

DO 15 I=2,NC
DO 10 J=1,I-1
CALL ESTACT(ID,I,J,EOKP,VX,KIJ)
10 CONTINUE
15 CONTINUE

30 CONTINUE

MAXIT=11111
! LOCAL PRESSURE AUTOMATICALLY INITIALIZED FROM BULK
PRESSURE
ANSWER=1
INIT=0

1000 CONTINUE

```

```

    RGAS=8.31434
    !
    !     X=1 IS THE BULK COMPOSITION (PURE COMPONENT)
    !
X(1) = 1

! SQUARE WELL POTENTIAL DISABLED
    WELLP = 0
    WELLD = 0

    EXCE=0
    AMTS=0
    ADSORB=0

!     SIGFF=0.
!     DO 12 I=1,NC
!           CALL SIGMAFIND(ID,I,SIGMA,NC)

!     SIGFF=(SIGMA(I)+SIGFF)

12    CONTINUE
!     SIGFF=SIGFF/NC
    SIGSS=3.4
    SIGFS=0.5*(SIGFF+SIGSS)
    ALPHASP=3.35/SIGFS

    LMNO=65.           ! IF YOU ADJUST THE INCREMENTS, REMEMBER
                      ! TO ADJUST THE PRESSURE AND
ADSORPTION           ! ARRAY DIMENSIONS AS WELL IF
NECESSARY

    DELP=BLKP/LMNO
    PB=0
    IFLAG=0
    ZLCL=0

    FACTOR=0.1

    J=1
    LOSFF=(H-SIGSS)/SIGFF

```

```

DO L=1,LMNO                ! BEGINNING OF PRESSURE CURVE LOOP

    PB=L*DELP

    PRESSURE(L) = PB    ! ARRAY OF PRESSURES

71    BULK=1
    LIQ=0
    FSQD=0.
    CALL FUGI(TC,RGAS,T,PB,X,NC,LIQ,FUGCCALC,ZVB,IER,RHOB,BULK,
&
        XA,FSQ,ALPHA,FSQD,LOSFF,ZOSFF)

    DO 29 I=1,NC
29    FKEEP(I)=FUGCCALC(I)
        ZKEEP=ZVB
        RHOKEEP=RHOB
    LIQ=1
    CALL FUGI(TC,RGAS,T,PB,X,NC,LIQ,FUGCCALC,ZVB,IER,RHOB,BULK,
&
        XA,FSQ,ALPHA,FSQD,LOSFF,ZOSFF)

    DO 203 I=1,NC
    IF(FUGCCALC(I).GT.FKEEP(I))THEN
    FUGCCALC(I)=FKEEP(I)
    ZVB=ZKEEP
    RHOB=RHOKEEP
    ENDIF
203    CONTINUE

    PLCL=PB

    DO 17 I=1,NC
17    FUGBULK(I)=X(I)*PB*FUGCCALC(I)

!    LAST MUST BE AN ODD NUMBER. IT IS THE NUMBER OF POINTS
GENERATED.
    LAST=199.

    EXCE=0
    AMTS=0
    ADSORB=0

    DELTAZ=(LOSFF-2.*FACTOR)/(LAST-1)
    ZOSFF=FACTOR-DELTAZ

```

```

DO 77 ISTEP=1, LAST
5   ZOSFF=ZOSFF+DELTAZ
    ZLCL=(ZOSFF*SIGFF+0.5*SIGSS)/SIGFS
    XI=(LOSFF*SIGFF+SIGSS/2.-ZOSFF*SIGFF)/SIGFS

    ITMAX=MAXIT
    DO 32 I=1, NC
      PSI1(I)=4.0*3.1415926*0.382*SIGFS*SIGFS*EPSFS*(-0.2      &
        /ZLCL**10+0.5/ZLCL**4+0.5/(ZLCL+ALPHASP)**4+0.5/(ZLCL+2.0* &
        ALPHASP)**4+0.5/(ZLCL+3.0*ALPHASP)**4+0.5/(ZLCL+4.0*ALPHASP) &
        **4)

      PSI2(I)=4.0*3.1415926*0.382*SIGFS*SIGFS*EPSFS*(-0.2    &
        /XI**10+0.5/XI**4+0.5/(XI+ALPHASP)**4+0.5/(XI+2.0*    &
        ALPHASP)**4+0.5/(XI+3.0*ALPHASP)**4+0.5/(XI+4.0*ALPHASP) &
        **4)

      PSI(I)=PSI1(I)+PSI2(I)

      SQWL=0.
      DIST1=(ZLCL-SIGSS/SIGFS/2.)*SIGFS
      DIST2=(XI-SIGSS/SIGFS/2.)*SIGFS
!     SQUARE WELL POTENTIAL FOR A SINGLE COMPONENT ONLY
      IF(DIST1.LE.(WELLD*SIGFF))SQWL=WELLP
      IF(DIST2.LE.(WELLD*SIGFF))SQWL=WELLP

      FUGLCL(I)=FUGBULK(I)*DEXP((PSI(I)+SQWL)/T)
32  CONTINUE          ! LN(f)=mu

      IF(J.EQ.1)THEN
        DO 50 I=1, NC
          IF(PSI(I).LT.-2500.)THEN
            ! WRITE(*,*) 'NO GOOD'
            p=0
            GOTO 5
          ELSE
            p=p+1
          endif
50  CONTINUE
      if(p.eq.1)then
        FACTOR=ZOSFF

      DELTAZ=(LOSFF-2*FACTOR)/(LAST-1)

```

```

        p=p+1
        ENDIF
    ENDIF
    J=2
    CALL
    BUBPL(TC, RGAS, T, NC, Y, IER, PLCL, FUG, RHO, XA, FUGLCL, LOSFF, ZOSFF)

```

6 continue

```

    DO 11 I=1,12
11  IF (IER(I).NE.0)IFLAG=1
    IF (IFLAG.EQ.1)WRITE(6,*)'IER',(IER(I),I=1,6)
    IF(IER(2).EQ.1)WRITE(*,*)'ERROR ALL VAPOR'
    IF(IER(3).EQ.1)WRITE(*,*)'ERROR ALL LIQUID'
    IF(IER(4).EQ.4)WRITE(*,*)'ERROR IN FUGI-NEG LOG CALCD'
    IF(IER(4).EQ.5)WRITE(*,*)'ERROR IN FUGI-FUGACITY OVERFLOWS'
    IF(IER(5).EQ.1)WRITE(*,*)'ERROR VAPOR AND LIQUID ROOTS CLOSE'
    IF(IER(6).EQ.1)WRITE(*,*)'ERROR VLE ITERATION NO CNVRG',ITMAX
    IF(IER(7).EQ.1)WRITE(*,*)'ERROR VLE ITERATION FAILED TO IMPROVE'
    IF(IER(8).EQ.1)WRITE(*,*)'ERROR IN TC,PC,OR X,Y'
    IF(IER(9).EQ.1)WRITE(*,*)'ERROR P SPECIFIED < 0'
    IF(IER(10).EQ.1)WRITE(*,*)'ERROR T SPECIFIED IS UNREASONABLE'
    IF(IER(11).EQ.1)WRITE(*,*)'ERROR MORE THAN 10 COMPONENTS'
        IF(IFLAG.EQ.1)PAUSE
        IF(IFLAG.EQ.1)STOP

!     LCLDENS IN MOL/CM3
44    LCLDENS(ISTEP)=RHO-RHOB
        RHOD(ISTEP)=RHO

        IF(ISTEP.EQ.(LAST))THEN
            DO 99 I=1,(LAST-2),2
                POSIT1=I
                POSIT2=I+1
                POSIT3=I+2
!     EXCESS IN MICROMOLES/M^2
            EXCE=SIGFS*DELTAZ*10**2*(LCLDENS(POSIT1)+4.*LCLDENS(POSIT2)+
            &
                LCLDENS(POSIT3))/6.+EXCE

            ADSORB=SIGFS*DELTAZ*10**2*(RHOD(POSIT1)+4.*RHOD(POSIT2)+
&

```

```

        RHOD(POSIT3))/6.+ADSORB
!      AMT DIVIDED BY 2 IN SLIT INTEGRATIONS
99     CONTINUE
!      AREA IN M^2/G, AMT IN MMOL/G
        AMTS = EXCE*AREA/1000.
    ENDF

77     CONTINUE

        ADSORP(L) = AMTS    ! ADSORPTION ARRAY

        END DO    ! END OF PRESSURE CURVE LOOP

82     CONTINUE

! NOTE: FOR REPEAT BP CALCULATIONS IT IS ASSUMED THAT
! BOOTSTRAPPING
! IS DESIRED. OTHERWISE, THE USER SHOULD ANSWER 'N' TO
! THE REPEAT QUESTION BELOW AND GO BACK THROUGH THE MAIN
! PROGRAM BEFORE PROCEEDING.

! THIS REPEAT STATEMENT HAS BEEN CHANGED TO START THE
! PROGRAM
! OVER. THE ABOVE NOTE IS INVALID.
! INIT=1

CLOSE(55)

END

```

## Arranger

```
C*****
  SUBROUTINE ARRANGE(R1,R2,R3)
  DOUBLE PRECISION R1,R2,R3
C   PROGRAM TO PUT 3 NUMBERS IN DESCENDING ORDER

  DO 20 J=1,3

    IF(R2.GT.R1) THEN
      TEMP=R1
      R1=R2
      R2=TEMP
    ENDIF

    IF(R3.GT.R2) THEN
      TEMP=R2
      R2=R3
      R3=TEMP
    ENDIF

  20 CONTINUE

  RETURN
  END
```

## Bubble Point Calculation

SUBROUTINE BUBPL(TC, RGAS, T, NC, Y, IER,  
1PLCL, FUG, RHO, XA, FUGLCL, LOSFF, ZOSFF)

C  
C REVISION DATE: FEB 93 (FOR ESD COMPATIBILITY)  
C REVISION DATE: JAN 92 SJS-FOR -VE PRESSURES  
C REVISION DATE: SEPTEMBER 5, 1985  
C PROGRAMMED BY: J.R. ELLIOTT, JR. (JAN. 1983)  
C  
C PURPOSE: CALCULATE BUBBLE POINT PRESSURE OF LIQUID BASED  
C ON TEMPERATURE AND LIQUID COMPOSITION.  
C  
C ARGUMENTS:  
C  
C INPUT:  
C TC() VECTOR CRITICAL TEMPERATURES OF THE COMPONENTS  
C PC() VECTOR CRITICAL PRESSURES OF THE COMPONENTS  
C ACEN() VECTOR ACENTRIC FACTORS OF THE COMPONENTS  
C ID() VECTOR STANDARD ID NUMBERS OF THE COMPONENTS  
C RGAS GAS CONSTANT (EG. 8.31434 CC-MPA/(GMOL-K) )  
C T ABSOLUTE TEMPERATURE  
C X() VECTOR MOLE FRACTIONS IN THE LIQUID PHASE  
C NC NUMBER OF COMPONENTS  
C INIT PARAMETER FOR SPECIFICATION OF WHETHER THE INITIAL  
GUESS  
C IS PROVIDED BY THE USER OR SHOULD BE CALCULATED.  
C INIT = 0 INITIAL GUESS FOR P CALCULATED BY PSTART  
C INIT = 1 INITIAL GUESS FOR P PASSED FROM CALLING ROUTINE  
C  
C INPUT/OUTPUT:  
C P OPTIONAL INPUT INITIAL GUESS/OUTPUT CALCULATED  
C ABSOLUTE PRESSURE  
C ITMAX INPUT MAXIMUM NUMBER OF ITERATIONS PERMITTED.  
C THE RECOMMENDED VALUE IS 50.  
C OUTPUT ITMAX IS SET TO THE NUMBER OF ITERATIONS  
PERFORMED  
C  
C OUTPUT:  
C Y() VECTOR MOLE FRACTIONS IN THE VAPOR PHASE  
C IER() VECTOR ERROR PARAMETERS  
C IER(1)=1 AT LEAST ONE OF IER(2)-IER(11) WAS NOT ZERO  
C IER(2)=1 LIQUID ROOT PASSED FROM FUGI WAS NOT REAL  
C ON LAST ITERATION

C IER(3)=1 VAPOR ROOT PASSED FROM FUGI WAS NOT REAL  
 C ON LAST ITERATION  
 C IER(4)=4,5,6 TERMINAL ERROR RETURNED FROM FUGI  
 CALCULATION  
 C THE NUMBER TELLS WHICH COMPONENT OF FUGI'S  
 C ERROR VECTOR WAS SIGNIFICANT  
 C =4 NEGATIVE LOG CALCULATED  
 C =5 LOG OF FUGACITY COEFFICIENT CAUSES OVERFLOW  
 C =6 ITERATION ON COMPRESSIBILITY FACTOR DID NOT  
 CONVERGE  
 C IER(5)=1 CALCULATIONS DETERMINED VAPOR & LIQUID ROOTS  
 EQUAL  
 C (TRIVIAL SOLUTION)  
 C IER(6)=1 FAILED TO CONVERGE IN ITMAX LOOPS  
 C IER(7)=1 AN ITERATION WAS PERFORMED WITH NO  
 IMPROVEMENT  
 C IN THE OBJECTIVE FUNCTION  
 C IER(8)=1 AN ELEMENT OF TC, PC, OR X WAS SPECIFIED  
 C INCORRECTLY.  
 C IER(9)=1 THE T SPECIFIED WAS LESS THAN ZERO.  
 C IER(10)=1 AN INITIAL GUESS FOR P WAS SPECIFIED BUT  
 C IT WAS UNACCEPTABLE.  
 C IER(11)=1 THE VALUE FOR NC WAS GREATER THAN 10.  
 C IER(12)=1 THE VALUE OF ITMAX WAS LESS THAN 1.  
 C  
 C NOTE: UNITS OF ALL THE INPUTS SHOULD BE  
 C CONSISTENT WITH UNITS OF RGAS. EXCEPT  
 C FOR THIS, THE USER MAY CHOOSE HIS OWN UNITS.  
 C  
 C REQD. ROUTINES:  
 C PSTART, FUGI, ESTACT, SRKNR  
 C  
 C SUBPROGRAM RESTRICTIONS:  
 C AS WRITTEN, THE MAXIMUM NUMBER OF COMPONENTS  
 C THAT CAN BE CONSIDERED IS TEN.  
 C  
 C GENERAL COMMENTS:  
 C THIS SUBROUTINE SOLVES THE OBJECTIVE FUNCTION GIVEN  
 C IN THE LITERATURE REFERENCE BY A SECANT ITERATION  
 C ON THE PRESSURE VARIABLE. THE SUBROUTINE CALLED  
 C FOR FUGACITY CALCULATIONS ("FUGI") CONFORMS TO THE  
 C SPECIFICATIONS OF THE SOAVE EQUATION OF STATE GIVEN  
 C IN PROCEDURE 8D1.1.  
 C  
 C METHOD RELIABILITY:

C THE AVERAGE ERRORS QUOTED BELOW ARE EXPECTED WHEN  
 USING  
 C THE CORRELATIONS OF BINARY INTERACTION COEFFICIENT GIVEN  
 C IN CHAP. 8 OF THE API TECHNICAL DATA BOOK.  
 C SYSTEM TYPE AVERAGE PERCENT ERROR IN P  
 C HYDROCARBON-HYDROCARBON 4.3  
 C HYDROCARBON-HYDROGEN SULFIDE 4.8  
 C HYDROCARBON-NITROGEN 14.0  
 C HYDROCARBON-CARBON MONOXIDE 7.6  
 C HYDROCARBON-CARBON DIOXIDE 7.4

C REFERENCES:

C ANDERSON, T.F.; PRAUSNITZ, J.M.; IND. ENG. CHEM. PROC.  
 C DES. DEV., 19:9-14, (1980).

C PROCEDURE 8D1.1 OF TECHNICAL DATA BOOK.

C\*\*\*\*\*

C IMPLICIT DOUBLE PRECISION(A-H,O-Z)  
 C DIMENSION TC(\*),Y(\*),IER(\*),XA1(10),XA2(10),ALPHA(NC)  
 C DOUBLE PRECISION RHO,RHOV,RHOL,FUGLCL  
 C COMMON/ETA/ETAL,ETA V,ZL,ZV  
 C COMMON/POSITION/ZLCL  
 C COMMON/LOCAL/DELTAZ  
 C COMMON FKEEP  
 C COMMON LOSFF,ZOSFF  
 C DOUBLE PRECISION FUG,CHECKL,PLCL,CHECKV,LOSFF,ZOSFF  
 C DIMENSION FUGCCALC(NC),IERF(6),FUGLCL(10),FUG(10),CHECKL(10),  
 C 1FUGL(10),FUGV(10),FUGCCALCL(NC),FUGCCALCV(NC),CHECKV(10),  
 C XA(10)

C  
 C CHECK INPUTS FOR ERRORS.

C  
 DO 5 I=1,12  
 IER(I)=0

5 CONTINUE

IF(NC.GT.10)IER(11)=1

DO 8 I=8,12  
 8 IF(IER(11).NE.0)IER(1)=1  
 IF(IER(1).NE.0)GOTO 95

```

C    IF(ISTART.EQ.0)THEN
101  DO 10 I=1,NC
10   FUGCCALC(I)=1
C    ISTART=1
C    ENDIF
C    MAX=ITMAX
C BEGINNING OF MAIN ITERATION LOOP

C3   DO 40 ITER=1,MAX
C    ITMAX=ITER
      BULK=0
C    Y(1)=1.
C    BULK IS USED TO TELL SUBROUTINE ATTCALC TO USE EITHER THE
BULK
C    ATTRACTIVE TERM OR THE LCL ATTRACTIVE TERM.
C    BULK=0 FOR YLCL
C    BULK=1 FOR YBULK

C CALCULATE VAPOR COMPOSITION AND ERROR IN OBJECTIVE
FUNCTION.

      SUMY=0
      DO 20 I=1,NC
        Y(I)=FUGLCL(I)/(FUGCCALC(I))/PLCL
        SUMY=SUMY + Y(I)
C    G=1.D0-SUMY
20   CONTINUE

C    IF(ITER.EQ.1)THEN

C      FOR FIRST ITERATION, OLD VALUES ARE COMPUTED.

C    POLD=PLCL
C    GOLD=G
C    PLCL=PLCL*.98D0
C    GO TO 26
C    ELSE

C FOR HIGHER ITERATIONS, A SECANT STEP IS TAKEN.

C    IF(G.EQ.GOLD)THEN
C      IER(7)=1
C      GO TO 86
C    END IF

```

```
C   CHNG=G*(PLCL-POLD)/(G-GOLD)
C   END IF
```

```
C   POLD=PLCL
C   GOLD=G
C33  PNEW=POLD - CHNG
C   PLCL=PNEW
C   IF (PLCL.LT.0.0) THEN
C     CHNG=CHNG/2.0
C     CHNG=.3*POLD
C     WRITE(6,*)'PLCL IS -VE IN BUBPL'
C     GOTO 33
C   ENDIF
```

```
C TEST FOR CONVERGENCE OF P AND Y. IF PRESSURE IS CONVERGED
C BUT Y IS NOT, SKIP RECALCULATION OF LIQUID FUGACITIES AT
C THE START OF THE NEXT ITERATION.
```

```
C   IF(DABS(SUMY-1).LE.1.D-9)THEN
```

```
C   GOTO 26
C   END IF
```

```
C NOT CONVERGED. GET NEW VAPOR FUGACITIES, CHECK FOR ERRORS.
```

```
26  DO 30 I=1,NC
     Y(I)=Y(I)/SUMY
```

```
30  CONTINUE
C   START OF INSERT
C   ALNFB=ALOG(FUGBULK(1))
C   DO 222 I=1,NC
C222 ALNFL=DLOG(FUGBULK(I))
C   FLCL=EXP(ALNFL)
```

```
C   Calculate local a
C   CALL ACALC(BETA,AB,ALCL,ZETA)
```

```
C           Using local parameters calculate VL and local density DENL.
C           A Newton-Raphson technique is used to converge the local fluid-
C           fluid pressure to the state where the local fluid-fluid fugacity
C           has the desired value. At each iteration in pressure, the local
C           volume (density) is determined. If zeta<1 the local density will
```

```

C          zero because no fluidmolecule will fit in the slit

C          IF (ZETA.LE.1) THEN
C              RHOL(L) = 0
C              GOTO 31
C          ENDIF

          TESTOLD=1E10
          LCOUNT=0
          FSQD=0.
          DO 25 J=1,400
C              CALL VFCAL(ALCL,B,T,PLCL,VLCL,FLCALC)
          SUMSQRS=0
          LIQ=1
          ! WRITE(60,*) 'PLCL = ',PLCL,' in BUBPL'
15      CALL FUGI(TC,RGAS,T,PLCL,Y,NC,LIQ,FUGCCALCL,
          1      ZL,IERF,RHOL,BULK,XA1,FSQ,ALPHA,FSQD,LOSFF,ZOSFF)
          IF(IERF(1).NE.0)THEN
          DO 35 DE=4,6
          IF(IERF(DE).EQ.1)IER(4)=DE
35      CONTINUE
          PAUSE
          END IF
          DO 103 I=1,NC
103     FUGL(I)=Y(I)*PLCL*(FUGCCALCL(I))

          SUMSQRSL=0
          DO 87 I=1,NC
          CHECKL(I)=(FUGLCL(I)-FUGL(I))**2
87      CONTINUE
          DO 88 I=1,NC
88      SUMSQRSL=CHECKL(I)+SUMSQRSL

          LIQ=0
16      CALL FUGI(TC,RGAS,T,PLCL,Y,NC,LIQ,FUGCCALCV,
          1      ZV,IERF,RHOV,BULK,XA2,FSQ,ALPHA,FSQD,LOSFF,ZOSFF)
          IF(IERF(1).NE.0)THEN
          DO 65 DE=4,6
          IF(IERF(DE).EQ.1)IER(4)=DE
65      CONTINUE
          PAUSE
          END IF

          DO 104 I=1,NC
104     FUGV(I)=Y(I)*PLCL*(FUGCCALCV(I))

```

```

SUMSQRSV=0
DO 94 I=1,NC
CHECKV(I)=(FUGLCL(I)-FUGV(I))**2
94 CONTINUE
DO 93 I=1,NC
93 SUMSQRSV=CHECKV(I)+SUMSQRSV

```

```

DO 105 I=1,NC
FUG(I)=FUGV(I)
RHO=RHOV
FUGCCALC(I)=FUGCCALCV(I)
SUMSQRS=SUMSQRSV
XA(I)=XA2(I)
Z=ZV
LIQ=0
IF(FUGL(I).LT.FUGV(I))THEN !CRITERIA IS NOW THE LOWEST
FUGACITY
91 FUG(I)=FUGL(I)
RHO=RHOV
FUGCCALC(I)=FUGCCALCL(I)
SUMSQRS=SUMSQRSV
XA(I)=XA1(I)
Z=ZL
LIQ=1
ENDIF
105 CONTINUE
DO 70 I=1,NC
X IF(FUG(I).LT.0) WRITE (*,*) 'FLCL= '
, FUG(I),PLCL
FR=FUGLCL(I)/FUG(I)
TEST=ABS(FR-1.)
C IF ITERATIONS ARE NOT CONVERGING, SUBDIVIDE THE
INTERVAL BY 2
C UP TO 3 TIMES.
IF(J.EQ.150)THEN
C PRINT*,PLCL,RHO,FSQ
C PRINT*,Z,LIQ,ALPHA(1),FUG(1),FUGLCL(1)
FSQD=0.3
GOTO 70
ENDIF
IF(J.EQ.250)THEN
FSQD=0.8
GOTO 70

```

```

ENDIF
if(j.eq.350)THEN
FSQD=1.
GOTO 70
ENDIF

      IF (TESTOLD.LT.TEST .AND. LCOUNT.LT.6.)THEN
                LCOUNT=LCOUNT + 1
2          PLCL=PLCL-DELP
                DELP=DELP*.3
                GOTO 23
      ENDIF
                LCOUNT = 0

                TESTOLD=TEST
      IF (TEST.LT.0.001) GOTO 86
C      USE A LIMITED NEWTON-RAPHSON TECHNIQUE BASED
ON RTdlnF = VdP.
C      THE FACTOR OF 1.2 LIMITS THE INITIAL STEP SIZE.
      IF (FR.LT.0) WRITE (*,*) 'FR= ', FR
      ALNFR=DLOG(FR)
      DELP=RGAS*T*ALNFR*RHO/1.2
      IF(-DELP.GT.PLCL) DELP=-0.5*PLCL

23     PLCL = PLCL+DELP
C     WRITE(*,*)'FUGLCL= ',FUGLCL(1), 'FUG= ',FUG(1)
      SUMY=0
      DO 200 K=1,NC
      Y(K)=FUGLCL(K)/(FUGCCALC(K))/PLCL
      SUMY=SUMY + Y(K)
C     G=1.D0-SUMY
200    CONTINUE

C     IF(ISTART.EQ.1)THEN
C     FOR FIRST ITERATION, OLD VALUES ARE COMPUTED.

C     POLD=PLCL
C     GOLD=G
C     PLCL=PLCL*.98D0
C     ISTART=ISTART+1
C     GOTO 9
C     ELSE

C FOR HIGHER ITERATIONS, A SECANT STEP IS TAKEN.

```

```

C   IF(G.EQ.GOLD)THEN
C     IER(7)=1
C     GO TO 86
C   END IF
C   CHNG=G*(PLCL-POLD)/(G-GOLD)
C   END IF

C   POLD=PLCL
C   GOLD=G
C33  PNEW=POLD - CHNG
C   PLCL=PNEW
C   IF (PLCL.LT.0.0) THEN
C     CHNG=CHNG/2.0
C     CHNG=.3*POLD
C     WRITE(6,*)'PLCL IS -VE IN BUBPL'
C     GOTO 33
C   ENDIF
9    DO 300 K=1,NC
    Y(K)=Y(K)/SUMY
300  CONTINUE

C   DO 901 L=1,NC
C901          FR=FUGLCL(L)/FUG(L)
C           TEST=ABS(FR-1.)
C   IF(TESTOLD.LT.TEST)THEN
C     CHNG=CHNG*.35
C     PLCL=PLCL - CHNG
C     GOTO 70
C   ENDIF

C           TESTOLD=TEST
C           IF (TEST.LT.0.001) GOTO 86

70   CONTINUE

25   CONTINUE
    WRITE (6,*) 'DID NOT CONVERGE, RHO=',RHO,' PLCL=',PLCL
C30   CONTINUE
END OF INSERT

C 70  CONTINUE

C   IF (SUMSQRS.LE.1.D-8) GOTO 86
C   ELSE
C     GOTO 40

```

```
C    END IF
C    IF(IERF(1).NE.0)THEN
C      DO 35 DE=4,6
C        IF(IERF(DE).EQ.1)IER(4)=DE
C35   CONTINUE
C
C    END IF
```

```
C    GOTO 86
C40  CONTINUE
```

```
C END OF MAIN ITERATION LOOP
```

```
C
```

```
C ONLY WAY FOR PROGRAM TO REACH THIS NEXT STATEMENT IS FOR
C NUMBER OF ITERATIONS TO EXCEED ITMAX
C THEREFORE INDICATE ERROR.
```

```
    IER(6)=1
```

```
C PERFORM FINAL ERROR CHECKS.
```

```
86  CONTINUE !WRITE(*,*)FUG(1),FUGLCL(1),PLCL
      IF(IERF(2).EQ.1)IER(2)=1
      IF(IERF(3).EQ.1)IER(3)=1
      DO 90 DE=2,7
        SAVEIT=PLCL
      IF(IER(DE).NE.0)IER(1)=1
90  CONTINUE
95  RETURN
    END
```

## Cubic

```
C &7 1 2 3 4 5 6 7 2
C *****
C * SUBROUTINE CUBIC *
C *****
C * THIS SUBROUTINE FINDS THE ROOTS OF A CUBIC EQUATION OF THE
C *
C * FORM  $X^3 + A2X^2 + A1X + A0 = 0$  ANALYTICALLY. *
C *****
C * VARIABLES *
C *****
C * A0 ----- THE ZEROETH ORDER TERM OF THE NORMALIZED CUBIC
C *
C * EQUATION *
C * A1 ----- THE FIRST ORDER TERM OF THE NORMALIZED CUBIC *
C * EQUATION *
C * A2 ----- THE SECOND ORDER TERM OF THE NORMALIZED CUBIC *
C * EQUATION *
C * C1 ----- THE COMPLEX ARGUMENT OF ROOT #1 OF THE EQUATION
C *
C * C2 ----- THE COMPLEX ARGUMENT OF ROOT #2 OF THE EQUATION
C *
C * C3 ----- THE COMPLEX ARGUMENT OF ROOT #3 OF THE EQUATION
C *
C * CCHECK --- THE SAME AS "CHECK" BUT CONVERTED TO COMPLEX
C *
C * NUMBER FORMAT *
C * CHECK ---  $Q^3 + R^2$ , USED TO CHECK FOR THE CASE OF THE *
C * SOLUTION AND IN FINDING THE ROOTS OF THE EQUATION, *
C * DOUBLE PRECISION *
C * DA0 ----- "A0" CONVERTED TO DOUBLE PRECISION *
C * DA1 ----- "A1" CONVERTED TO DOUBLE PRECISION *
C * DA2 ----- "A2" CONVERTED TO DOUBLE PRECISION *
C * ES1 ----- AN INTERMEDIATE CALCULATION TO USED IN THE *
C * CALCULATION OF "S1" *
C * ES2 ----- AN INTERMEDIATE CALCULATION TO USED IN THE *
C * CALCULATION OF "S2" *
C * IFLAG --- A FLAG TO INDICATE THE CASE OF THE SOLUTION OF THE
C *
C * EQUATION: =1 ONE REAL + TWO COMPLEX ROOTS, *
C * =2 ALL REAL ROOTS, AT LEAST TWO THE SAME *
C * =3 THREE DISTINCT REAL ROOTS *
C * P1 ----- AN INTERMEDIATE SUM USED IN THE CALCULATION OF *
C * "SS1" *
C * P2 ----- AN INTERMEDIATE SUM USED IN THE CALCULATION OF *
```

```

C *      "SS2"
C * Q ----- AN INTERMEDIATE SUM USED IN CALCULATING "CHECK" *
C * R ----- AN INTERMEDIATE SUM USED IN CALCULATING "CHECK" *
C * R1 ----- THE REAL ARGUMENT OF ROOT #1 OF THE EQUATION *
C * R2 ----- THE REAL ARGUMENT OF ROOT #2 OF THE EQUATION *
C * R3 ----- THE REAL ARGUMENT OF ROOT #3 OF THE EQUATION *
C * RECK ---- THE SAME AS "CHECK", BUT SINGLE PRECISION REAL *
C * S1 ----- AN INTERMEDIATE VALUE USED TO FIND THE ROOTS OF *
C *      THE EQUATION, COMPLEX NUMBER *
C * S2 ----- AN INTERMEDIATE VALUE USED TO FIND THE ROOTS OF *
C *      THE EQUATION, COMPLEX NUMBER *
C * SS1 ---- THE SAME AS S1 BUT DOUBLE PRECISION REAL *
C * SS2 ---- THE SAME AS S2 BUT DOUBLE PRECISION REAL *
C * Z1 ----- ROOT #1 OF THE EQUATION, COMPLEX NUMBER *
C * Z2 ----- ROOT #2 OF THE EQUATION, COMPLEX NUMBER *
C * Z3 ----- ROOT #3 OF THE EQUATION, COMPLEX NUMBER *
C *****

```

```

SUBROUTINE CUBIC(A2,A1,A0,R1,R2,R3,C1,C2,C3,IFLAG)

```

```

    DOUBLE PRECISION A2,A1,A0,R1,R2,R3

```

```

    DOUBLE PRECISION CHECK,DA0,DA1,DA2,P1,P2,Q,R,SS1,SS2

```

```

    COMPLEX ES1,ES2,S1,S2,Z1,Z2,Z3,CCHECK

```

```

    DA0 = DBLE(A0)

```

```

    DA1 = DBLE(A1)

```

```

    DA2 = DBLE(A2)

```

```

    Q = DA1/3.D00 - DA2*DA2/9.D00

```

```

    R = (DA1*DA2 - 3.D00*DA0)/6.D00 - (DA2/3.D00)**3

```

```

    CHECK = Q**3 + R*R

```

```

    IF (CHECK.GT.0.0) THEN

```

```

        IFLAG = 1

```

```

        P1 = R + DSQRT(CHECK)

```

```

            IF(P1.EQ.0.0)P1=1.D-7

```

```

        P2 = R - DSQRT(CHECK)

```

```

            IF(P1.EQ.0.0)P1=1.D-7

```

```

        IF (P1.LT.0.0) THEN

```

```

            SS1 = -DEXP((DLOG(-1.D00*P1))/3.D00)

```

```

        ELSE

```

```

            SS1 = DEXP((DLOG(P1))/3.D00)

```

```

        ENDIF

```

```

            IF(P2.EQ.0.0)P2=1.D-7

```

```

        IF (P2.LT.0.0) THEN

```

```

            SS2 = -DEXP((DLOG(-1.D00*P2))/3.D00)

```

```

        ELSE

```

```

            SS2 = DEXP((DLOG(P2))/3.D00)

```

```

        ENDIF

```

```

    R1 = SS1 + SS2 - DA2/3.D00

```

```

    R2 = -(SS1 + SS2) - DA2/3.D00

```

```

R3 = R2
C1 = 0.0
C2 = (SQRT(3.))*(SS1 - SS2)/2.D00
C3 = -C2
ELSE IF (CHECK.LT.0.0) THEN
  IFLAG = 3
  RR = 1.*R
  RECK = 1.*CHECK
  CCHECK = CMPLX(RECK,0.0)
  ES1 = CLOG(RR + CSQRT(CCHECK))/3.
  ES2 = CLOG(RR - CSQRT(CCHECK))/3.
  S1 = CEXP(ES1)
  S2 = CEXP(ES2)
  Z1 = (S1 + S2) - A2/3
  Z2 = -(S1 + S2)/2 - A2/3 + (CMPLX(0.0,3**.5))*(S1 - S2)/2
  Z3 = -(S1 + S2)/2 - A2/3 - (CMPLX(0.0,3**.5))*(S1 - S2)/2
  R1 = REAL(Z1)
  R2 = REAL(Z2)
  R3 = REAL(Z3)
  C1 = 0.0
  C2 = C1
  C3 = C1
ELSE
C *****
C * IF THE ROOTS OF THE EQUATION ARE VERY, VERY SMALL AND
VERY, *
C * VERY CLOSE TOGETHER, THIS SUBROUTINE MAY ERRONEOUSLY
REPORT *
C * THAT THE EQUATION HAS ONLY ONE ROOT NEAR ZERO *
C *****
  IFLAG = 2
  IF (R.LT.0.0) THEN
    SS1 = -DEXP((DLOG(-1.D00*R))/3.D00)
  ELSE IF (R.EQ.0.0) THEN
    SS1 = 0.0
  ELSE
    SS1 = DEXP((DLOG(R))/3.D00)
  ENDIF
  SS2 = SS1
  R1 = SS1 + SS2 - DA2/3.D00
  R2 = -(SS1 + SS2)/2 - DA2/3.D00
  R3 = R2
  C1 = 0.0
  C2 = C1
  C3 = C2
ENDIF

```

RETURN  
END  
C &7 1 2 3 4 5 6 7 2

## Fugacity Calculation

```
C   C$FUGI.FOR
C   LATEST REVISION : 9/94 jre
C       : 1/96 (switched to chempot, ADDED POLYETHYLENE jre)
c       7/96 PS, PPO, PEO, PIB (ram natarajan)
      SUBROUTINE
FUGI(TC, RGAS, T, P, X, NC, LIQ, FUGC, Z, IER, RHO, BULK, XA, FSQ,
      1ALPHA, FSQD, LOSFF, ZOSFF)
      IMPLICIT DOUBLE PRECISION(A-H, K, O-Z)
      PARAMETER(NMX=10)
      DIMENSION TC(*), X(*), FUGC(NC), IER(6)
      1
, YQVIJ(NMX, NMX), KVE(NMX), YQVI(NMX), Y(NMX, NMX), EOK(NMX, NMX)
      1 , CVI(NMX), CVIJ(NMX, NMX), QV(NMX, NMX), XA(NMX)
      COMMON/ESD/KCSTAR, DH, C, Q, VX, VLK, ND, EOKP
      COMMON/ETA/ETAL, ETAV, ZL, ZV
      COMMON/DEPFUN/DUONKT, DAONKT, DSONK, DHONKT
      COMMON/POSITION/ZLCL
      COMMON/CONSTK/KIJ(NMX, NMX), INITIAL
      COMMON FKEEP
C   COMMON LOSFF, ZOSFF
      DIMENSION
EOKP(NMX), KCSTAR(NMX), DH(NMX), C(NMX), Q(NMX), VX(NMX)
      & , ND(NMX), k1(nmx), VLK(NMX), ALPHA(NMX), RALPHA(NMX)
      DOUBLE PRECISION RHO, P, Z, ZOLD, B, ETA, LOSFF, ZOSFF
      DOUBLE PRECISION FSQ, F, A2, A1, A0, R1, R2, R3, FSQD
C   ND IS THE DEGREE OF POLYMERIZATION OF EACH SPECIES
C   EOKP IS THE DISPERSE ATTRACTION OVER BOLTZ k FOR PURE SPECIES
C   KCSTAR IS THE DIMENSIONLESS BONDING VOLUME FOR PURE
C   DH IS THE REDUCED BONDING ENERGY
C   C, Q, VX ARE THE PURE COMPONENT EOS PARAMETERS
C   KIJ IS THE BINARY INTERACTION COEFFICIENT
C   Z IS PV/NoKT HERE
C   IER = 1 - AT LEAST ONE ERROR
C       2 - TOO MANY ALPHA ITERATIONS
C       3 -
C       4 - ERROR IN ALPHA CALCULATION, SQRT(ALPHA) OR ITERATIONS
C       5 -
C       6 - TOO MANY Z ITERATIONS
C
      DATA K10, K2, ZM/1.7745, 1.0617, 9.5/
      TRY=ZLCL
      IF(INITIAL.EQ.0)THEN
C   WRITE(*, *)'INPUT k11'
```

```

C  READ(*,*)k11
  DO 1 I=1,NC
    K1(I)=K10
C  POLYMER DATA WAS REMOVED FROM THIS AREA!
1  CONTINUE
  INITIAL=1
  END IF
    DATA TBASE,TSLOPE/400,0/
    DO 11 I=1,NC
11  FUGC(I)=1
    IER(2)=0
    IER(3)=0
    YQVM=0.0
    VM=0.0
    CVM=0
    K1YVM=0
    DO 30 I=1,NC
      IF(X(I).LT.0)PAUSE'ERROR IN FUGI, Xi<0'
      DO 40 J=1,NC

        EOK(I,J)=DSQRT(EOKP(I)*EOKP(J))*
&      ( 1-KIJ(I,J)*(1+(T-TBASE)/TBASE*TSLOPE) )
        CALL ATTCALC(EOK, Y,I,J,T,BULK,LOSFF,ZOSFF)
C Y(I,J) AND EOK(I,J) REPRESENT THE LOCAL TERMS CALCULATED IN
ATTCALC
      QV(LJ) = (Q(I)*VX(J) + Q(J)*VX(I)) / 2.0
      YQVIJ(LJ)=QV(LJ)*Y(I,J)
      CVIJ(LJ) = (C(I)*VX(J) + C(J)*VX(I)) / 2.0
      YQVM=YQVM+YQVIJ(LJ)*X(I)*X(J)
      CVM = CVM + CVIJ(LJ)*X(I)*X(J)
40  CONTINUE
c    kcstar(1)=0.075
      KVE(I)=KCSTAR(I)*VX(I)*( DEXP(DH(I)/T*TC(I))-1 )
      VM=VM+X(I)*VX(I)
      K1YVM=K1YVM+X(I)*K1(I)*Y(I,I)*VX(I)

30  CONTINUE

  IF(K1YVM.eq.0)write(6,*)'k1yvm in fugi=',k1yvm

C  INITIATE SECANT ITERATION ON RHO

  PORT=P/RGAS/T
  PVMORT=PORT*VM

C  GUESS FOR RHO

```

```

C   ETA=PVMORT
C   IF(LIQ.EQ.1)ETA=.52
C   RHO=ETA/VM
C   IF(LIQ.EQ.0)RHO=PORT
C   WRITE(6,*)'Z IN FUGI ',Z

```

C ALPSOL WILL USE THIS VALUE OF RHO TO CALCULATE A NEW VALUE OF RHO

```

C       CALL ALPSOL(X,NC,KVE,ND,VM,
C   &           RHO,ZASSOC,XA,RALPH,FASSOC,IER)
C39    CONTINUE

```

```

C   IF(IER(4).EQ.1)GOTO 86
C   ZREP=4*CVM*RHO/(1-1.9D0*VM*RHO)
C   ZATT=-ZM*YQVM*RHO/(1+K1YVM*RHO)
C   Z=(1+ZREP+ZATT+ZASSOC)

```

```

C   RHOLD=RHO
C   ERROLD=PORT-RHO*Z
C   RHO=RHO/1.05
C   IF (RHO.LT.0) WRITE(6,31)LIQ
C   NITER=0

```

```

C100  NITER=NITER+1

```

```

C   IF(NITER.GT.2500)GO TO 86

```

```

C   IER(2)=0

```

```

C   IER(3)=0

```

```

C   ETA=RHO*VM

```

```

C10   CALL

```

```

ALPSOL(X,NC,KVE,ND,VM,RHO,ZASSOC,XA,RALPH,FASSOC,IER)

```

```

C   IF(IER(4).EQ.1)GOTO 86

```

```

C   ZREP=4*CVM*RHO/(1-1.9D0*VM*RHO)

```

```

C   ZATT=-ZM*YQVM*RHO/(1+K1YVM*RHO)

```

```

C   Z=(1+ZREP+ZATT+ZASSOC)

```

```

C   ERR=PORT-RHO*Z

```

```

C   CHNG=ERR/(ERR-ERROLD)*(RHO-RHOLD)

```

```

C   RHOLD=RHO

```

```

C   ERROLD=ERR

```

```

C   RHO=RHO-CHNG

```

```

C   IF(DABS(CHNG/RHO).GT.1.D-10)GO TO 100

```

```

C   WRITE(*,*)'ETA,Z',ETA,Z

```

```

C  WRITE(*,*)'ZREP,ZATT',ZREP,ZATT
C  IF (RHO.LT.0) WRITE(6,31)LIQ
C  ITERATION ON RHO HAS CONCLUDED.  GET DEPARTURES AND
FUGACITY COEFFS.
      IF(FSQD.GT.0.01)THEN
      FSQ=FSQD
      GOTO 2
      ENDIF
      FSQ=0.03
      IF(LIQ.EQ.1)FSQ=0.8
2     ZOLD=5.

      DO 50 ITER=1,1000
      B=VM*P/RGAS/T

      A2=K1YVM*P/RGAS/T-1.-1.9*B+FSQ

      A1=-1.9*K1YVM/VM*B**2-K1YVM*B/VM+1.9*B-4*CVM*B/VM+
      1ZM*YQVM*P/RGAS/T+FSQ*K1YVM*P/(RGAS*T)

      A0=1.9*K1YVM/VM*B**2-4*K1YVM*CVM/VM/VM*B**2-
      ZM*1.9*YQVM/VM*B**2

      CALL CUBIC(A2,A1,A0,R1,R2,R3,C1,C2,C3,IFLAG)

      IF(IFLAG.NE.1) THEN
      CALL ARRANGE(R1,R2,R3)
      ZV=(R1)
      ZL=(R3)

      IF(LIQ.EQ.1)THEN
      RHO=P/ZL/RGAS/T
      ETA=VM*RHO
      DO 81 I=1,NC
      ALPHA(I)=KVE(I)/VM*ETA/(1-1.9*ETA)
      IF(ALPHA(I).LT.0.)THEN
      FSQ=FSQ*.3
      GOTO 50
      ENDIF
81    CONTINUE
      CALL FCALC(X,NC,ALPHA,FSQ,F,XA,RALPHA,ND)
      Z=ZL
      ELSE

```

```

RHO=P/ZV/RGAS/T
ETA=VM*RHO
DO 82 I=1,NC
ALPHA(I)=KVE(I)/VM*ETA/(1-1.9*ETA)
IF(ALPHA(I).LT.0.)THEN
FSQ=FSQ/2.
GOTO 50
ENDIF
82 CONTINUE
      CALL FCALC(X,NC,ALPHA,FSQ,F,XA,RALPHA,ND)
Z=ZV
ENDIF

ELSE
Z=R1
RHO=P/Z/RGAS/T
ETA=VM*RHO
DO 83 I=1,NC
ALPHA(I)=KVE(I)/VM*ETA/(1-1.9*ETA)
IF(ALPHA(I).LT.0.)THEN
FSQ=FSQ/2.
GOTO 50
ENDIF
83 CONTINUE
      CALL FCALC(X,NC,ALPHA,FSQ,F,XA,RALPHA,ND)
ENDIF
COMPARE=DABS(ZOLD/Z-1.)
IF(COMPARE.LE.0.001)GOTO 52
ZOLD=Z
50 CONTINUE
51 WRITE(*,*)'WARNING--NO. ITERATIONS EXCEEDED! (FUGI)'
WRITE(*,*)'LIQ = ',LIQ
WRITE(*,*)'Z = ',Z
WRITE(*,*)'ZV = ',ZV
WRITE(*,*)'ZL = ',ZL
WRITE(*,*)'COMPARE = ',COMPARE
WRITE(*,*)'P = ',P,'in FUGI'
WRITE(*,*)'T = ',T
WRITE(*,*)'ITER = ',ITER
IF(ETA.GT.0.52.OR.ETA.LT.0.)THEN
PRINT*, 'ETA= ',ETA
ETA=DABS(ETA/10.)
RHO=ETA/VM
Z=.9
DO 19 L=1,NC
XA(L)=.9

```

```

      FUGC(L)=.9
19  CONTINUE
      ENDIF
52  CONTINUE
C   WRITE(52,*)'Y=',Y

      ZREP=4*CVM*RHO/(1-1.9D0*VM*RHO)
      ZATT=-ZM*YQVM*RHO/(1+K1YVM*RHO)
C   Z=(1+ZREP+ZATT+ZASSOC)

      ETA=RHO*VM
      DO 77 I=1,NC
          YQVI(I)=0.D0
          CVI(I)=0.D0
77  CONTINUE

      ASSOC=0
      UNUMER=0
      UDENOM=1
      UATT=0
      DO 90 I=1,NC
          ASSOC=ASSOC+X(I)*ND(I)*( 2*DLOG(XA(I))+1-XA(I) )
          UATT=UATT+X(I)*VX(I)*EOK(I,I)/T*(Y(I,I)+K2)*K1(I)
          UFACTI=X(I)*ND(I)*RALPHA(I)*XA(I)*(2-XA(I))
          UDENOM=UDENOM+X(I)*ND(I)*(RALPHA(I)*XA(I))**2
          EBETHI=DH(I)/T*TC(I)
          IF(EBETHI.GT.1.D-5)THEN
              EBETHI=(EXP(EBETHI)-1)/EBETHI
          ELSE
              EBETHI=1
          END IF
          DO 80 J=1,NC
              EBETHJ=DH(J)/T*TC(J)
              IF(EBETHJ.GT.1.D-5)THEN
                  EBETHJ=(EXP(EBETHJ)-1)/EBETHJ
              ELSE
                  EBETHJ=1
              END IF
              QIJ=(EXP(DH(J)/T*TC(J))/EBETHJ+EXP(DH(I)/T*TC(I))/EBETHI)/2
              UNUMER=UNUMER+UFACTI*X(J)*ND(J)*RALPHA(J)*XA(J)*QIJ
              YQVI(I)=YQVI(I)+YQVIJ(I,J)*X(J)
              CVI(I)=CVI(I) + CVIJ(I,J)*X(J)
80  CONTINUE
90  CONTINUE
      IF (IER(2).NE.0)WRITE(6,*)'ERROR IN LIQUID PHASE IN ALPSOL'
      IF (IER(3).NE.0)WRITE(6,*)'ERROR IN VAPOR PHASE IN ALPSOL'

```

```

ETA=RHO*VM
IF (LIQ.EQ.1) THEN
  ETAL=ETA
  ZL=Z
ELSE
  ETAV=ETA
  ZV=Z
ENDIF

C   QUEST=1-1.9D0*ETA
C   IF (QUEST.LT.0)WRITE(6,*)'WARNING! (1-1.9*ETA) IS -VE IN FUGI'

      DO 120 I=1,NC
      FREP=-4.D0/1.9D0*DLOG(1.0-1.9*ETA)*CVM/VM
      FUGREP=FREP*( 2*CVI(I)/CVM-VX(I)/VM ) + ZREP*VX(I)/VM

      FATT=-ZM*YQVM/K1YVM*DLOG(1.D0+K1YVM*RHO)
      FUGATT=ZATT*K1(I)*Y(I,I)*VX(I)/K1YVM+
+      FATT*( 2*YQVI(I)/YQVM-K1(I)*Y(I,I)*VX(I)/K1YVM )

      FUGASN=-1.9D0*RHO*VX(I)*FSQ/(1.D0-1.9D0*ETA)
      FUGBON=2*ND(I)*DLOG( XA(I) )+FUGASN

C   IF (Z.LT.0.0)THEN
C     WRITE(6,*)'WARNING! Z NEGATIVE IN FUGI!'
C   ENDIF

      FUGC(I)=FUGREP+FUGATT+FUGBON-DLOG(Z)
      FUGC(I)=DEXP(FUGC(I))

120  CONTINUE

      UATT=-ZM*YQVM*RHO/(1+K1YVM*RHO)*UATT/K1YVM
      UASSOC=-UNUMER/UDENOM
      DUONKT=UATT+UASSOC
      DAONKT=FREP+FATT+ASSOC-DLOG(Z)
      DSONK =DUONKT-DAONKT
      DHONKT=DUONKT+Z-1

      RETURN

86  WRITE(6,686)
31  FORMAT(1X,'LIQ=',1X,I1,2X,',','WARNING! RHO (1) -VE IN FUGI')
33  FORMAT(1X,'LIQ=',1X,I1,2X,',','WARNING! RHO (2) -VE IN FUGI')

```

```
686 FORMAT(' ERROR IN FUGI. ')
C   IF(NITER.GE.2500)THEN
C   WRITE(*,*)'TOO MANY Z ITERATIONS'
C   IER(6)=1
C   END IF
IF(IER(4).EQ.1) WRITE(*,*)'ERROR IN ALPSOL'
IER(1)=1

RETURN
END
```

## Appendix C: BINARY MIXTURE ADSORPTION PROGRAM

```

C   PROGRAM BINARY ADSORPTION
C
C   DISCLAIMER
C   This code is distributed for educational purposes only.
C   The code is not to be sold.
C   There is no warranty or guarantee of suitability for any
C application.
C   By using the code the user agrees to these terms.
C
C   Note: BULK PHASE MUST BE A GAS
C   Define Psi as a state function
C   Use a 10-4 potential where PSI is the negative of the
C intermolecular potential.
C   SIGGS1 and SIGGS2 are sigma fluid-wall for components 1 & 2, in Angstroms.
C   EPSGS1 & 2 are the fluid-wall potential in K
C   EXC1 & 2 are the excess in micro mol/m2
C   AMT1 & 2 are the amount adsorbed in mmol/g
C   Y1 & 2 are the compositions of the two components in the adsorbed phase
C   P1 & 2 are the fugacity coefficients for the two components
C   F1 & 2 are the fugacities
C   p is the pressure in Mpa
C   TC, PC and W represent the critical temperature, pressure and omega's
C   ZETA = (slit width in A)/sigmaGG : entire slit width in terms
C of the quantity of "diameters" of fluid particles
*   This program is to calculate the adsorption in a mixture for
*   a slit

REAL K12b,K12,V1,V2,VV1,VV2,LWIDTH
CHARACTER RFILE*80
INTEGER H,K,IFLAG,L,NROOT

C   Function statements for the Lennard-Jones potentials
C   PSI1 (potential) for component A resulting from wall 1
PSI1(ETA)=4.0*3.1415926*0.382*SIGGS1*SIGGS1*EPSGS1*(-0.2
1/ETA**10+0.5/ETA**4+0.5/(ETA+ALPHA)**4+0.5/(ETA+2.0*
*ALPHA)**4+0.5/(ETA+3.0*ALPHA)**4+0.5/(ETA+4.0*ALPHA)
***4)

C   PSI2 (potential) for component B resulting from wall 1
PSI2(ETA)=4.0*3.1415926*0.382*SIGGS2*SIGGS2*EPSGS2*(-0.2
1/ETA**10+0.5/ETA**4+0.5/(ETA+ALPHA)**4+0.5/(ETA+2.0*
*ALPHA)**4+0.5/(ETA+3.0*ALPHA)**4+0.5/(ETA+4.0*ALPHA)
***4)

```

- C PSI3 (potential) for component A resulting from wall 2  

$$\text{PSI3(XI)}=4.0*3.1415926*0.382*\text{SIGGS1}*\text{SIGGS1}*\text{EPSGS1}*(-0.2$$

$$1/\text{XI}^{10}+0.5/\text{XI}^4+0.5/(\text{XI}+\text{ALPHA})^4+0.5/(\text{XI}+2.0*$$

$$*\text{ALPHA})^4+0.5/(\text{XI}+3.0*\text{ALPHA})^4+0.5/(\text{XI}+4.0*\text{ALPHA}$$

$$^{4})$$
- C PSI4 (potential) for component B resulting from wall 2  

$$\text{PSI4(XI)}=4.0*3.1415926*0.382*\text{SIGGS2}*\text{SIGGS2}*\text{EPSGS2}*(-0.2$$

$$1/\text{XI}^{10}+0.5/\text{XI}^4+0.5/(\text{XI}+\text{ALPHA})^4+0.5/(\text{XI}+2.0*$$

$$*\text{ALPHA})^4+0.5/(\text{XI}+3.0*\text{ALPHA})^4+0.5/(\text{XI}+4.0*\text{ALPHA}$$

$$^{4})$$
- C Total potential for component A  

$$\text{PSIA(ETA)}=\text{PSI1(ETA)}+\text{PSI3(XI)}$$
- C Total potential for component B  

$$\text{PSIB(ETA)}=\text{PSI2(ETA)}+\text{PSI4(XI)}$$
- C Fluid-fluid center-to-center distance averaged between components  
 C **\*\*Note: according to Reid,Prausnitz,and Poling,**  
 C Methane SIGFF=3.758, Ethylene SIGFF=4.163  

$$\text{SIGFF} = 4$$
- C Solid-solid (carbon) center-to-center distance  

$$\text{SIGWW} = 3.4$$

$$\text{SIGGS1}=(\text{SIGFF}+\text{SIGWW})/2$$

$$\text{SIGGS2}=\text{SIGGS1}$$

$$\text{ALPHA}=3.35/\text{SIGGS1}$$
- C Gas Constant  

$$\text{R} = 8.314$$
- C Component critical properties  
 C Ethylene  
 C TC1=282.4  
 C PC1=5.032  
 C W1=0.085  
 C ethane  
 C TC2=305.4  
 C PC2=4.880  
 C W2=0.099  
 C Mixing parameters (from experimental data)  
 C CO2-TOLUENE  

$$\text{K12b}=.1058$$
  
 C METHANE-ETHYLENE  
 C 
$$\text{K12b}=.0209$$
  
 C METHANE-ETHANE

C K12b=.0094

C Unit conversion from MPa to Pa  
 $PC2 = 1000000 * PC2$   
 $PC1 = 1000000 * PC1$

C User interface; HWIDTH is slit width in angstroms  
 2 PRINT\*, 'ENTER T(K), P(MPA),EPS1, EPS2, HWIDTH'  
 READ\*, T,P,EPSGS1,EPSGS2,HWIDTH  
 $K12=K12b$   
 $LWIDTH=HWIDTH*1.0-SIGWW$   
 $ZETA=LWIDTH*1.0/SIGFF$

C Conversion to Pa  
 $P=1000000 * P$

C Mole fraction of component 1  
 3 PRINT\*, 'ENTER V1'  
 READ\*, V1

C Initial adsorption values set to 0  
 $EXC1=0.0$   
 $EXC2=0.0$   
 $AMT1=0.0$   
 $AMT2=0.0$

WRITE(\*,\*) 'Output will be submitted to test.txt and test2.txt'  
 OPEN(UNIT=2,NAME='test.txt',TYPE='UNKNOWN')  
 OPEN(UNIT=5,NAME='test2.txt',TYPE='UNKNOWN')  
 OPEN(UNIT=12,NAME='test3.txt',TYPE='UNKNOWN')  
 WRITE(\*,\*)  
 WRITE(\*,\*) 'Enter any letter to proceed with calculations.'  
 READ(\*,\*) RFILE

C Universal mole fraction variables: V1 and V2

C Bulk mole fraction variables: V1IN and V2IN  
 $V2 = 1 - V1$   
 $V1IN = V1$   
 $V2IN = V2$

C Finite difference specifications for composition

C DDV1: comp. 1 mole fraction change, DDV2: comp. 2  
 $DDV1 = 1E-2$   
 $DDV2 = 1E-2$

C Reduced temperatures

C  $TR1 = T/TC1$

C  $TR2 = T/TC2$

\* SET DELTA P FOR PARTIAL DERIVATIVES; finite difference spec.

C DDP=.01\*P

C -----BULK CALCULATIONS-----

\* CALCULATE COMPRESSIBILITY FACTOR (Z)

\* CALCULATE A1,A2, THEN A

C Tabulated ESD parameters; b (cm\*\*3/mol); EPS1ff (K)

C c,q dimensionless

C See ESDparms file

C Component 1: Ethylene

C Component 2: Ethane

C Ethylene

C EPS2ff=210.275

C c2=1.305

C q2=1.581

C b2=15.013

C Ethane

C EPS2ff=220.429

C c2=1.3552

C q2=1.6765

C b2=16.716

C Methane

C EPS1ff=178.082

C c1=1.0382

C q1=1.0728

C b1=10.863

C Toluene

EPS1ff=332.752

c1=1.971

q1=2.849

b1=36.227

C Carbon Dioxide

EPS2ff=178.269

c2=1.832

q2=2.585

b2=10.534

C Fsq is association parameter not currently being applied

Fsq=0.0

C Carbon surface area (m\*\*2/g)

Area=1300.

C Convert b1 and b2 from cm\*\*3/mole to m\*\*3/mole

b1=b1/10\*\*6

b2=b2/10\*\*6

```

C   Calculation of Y(bulk)
C   Y1b: bulk Y for component 1
C   Y2b: bulk Y for component 2
C   Y12b: intercomponent bulk Y
      CALL YCALC(EPS1ff,T,Y1b)
      CALL YCALC(EPS2ff,T,Y2b)
      EPS12=((EPS1ff*EPS2ff)**.5)*(1-K12b)
      CALL YCALC(EPS12,T,Y12B)
      EPS12s=((EPS1ff*EPS2ff)**.5)*(1-K12)
      CALL YCALC(EPS12s,T,Y12Bs)

C   Mixing of bulk parameters b (bb),c (cb), and q (qb)
      CALL BCQMIX(V1IN,V2IN,b1,b2,c1,c2,q1,q2,Y1b,Y2b,Y12b,bb,cb,
1  qYbb,Ybb)
      WRITE(*,*)"Returned from BCQMIX"
      WRITE(*,*)"bb = ",bb

C   Variables necessary for cubic calculation
      capBb=(bb*P)/(R*T)
      capqYBb=qYbb*P/R/T
      capYBb=Ybb*P/R/T

C   R1, R2, and R3: root values for Z (compressibility)
      WRITE(*,*)"Calling SCUBIC"
      CALL SCUBIC(capBb,cb,Fsq,capqYBb,capYBb,R1,R2,R3,IFLAG)
      IF(IFLAG.EQ.1) Z=R1
      IF(IFLAG.EQ.2) THEN
        Z=R1
        IF(R2.GT.R1) Z=R2
      END IF
      IF(IFLAG.EQ.3) THEN
        CALL ARRANGE(R1,R2,R3)
        Z=R1
      END IF

C   DENB is bulk molar density
      DENB=P/Z/R/T
      WRITE(*,*)"DENB = ",DENB
      WRITE(*,*)"1.9N = ",DENB*bb*1.9

C   Fugacity Coefficient Calculation (P1,P2)
C   Component 1
      WRITE(*,*)"Calling FUG for P1 bulk"
      CALL FUG(cb,c1,bb,b1,b2,Y1b,Y12b,DENB,V1IN,V2IN,q1,q2,qYbb,Ybb,
1  Z,P1)

```

```

C   Component 2
    WRITE(*,*)"Calling FUG for P2 bulk"
      CALL FUG(cb,c2,bb,b2,b1,Y2b,Y12b,DENB,V2IN,V1IN,q2,q1,qYbb,Ybb,
1     Z,P2)
C   WRITE(*,*) 'A & B star ',AS,BS,'FUG',P1,P2

```

```

C   Conversion to MPa from Pa
    PBULK=P/1000000

```

```

    WRITE(2,*) 'T =',T,' K ',P =', PBULK,' MPa'
    WRITE(2,*) 'BULK DEN =', DENB,' gmol/m^3',' Width = ',ZETA
    WRITE(2,*)'Epsilon 1 & 2 =', EPSGS1,EPSSGS2
    WRITE(2,*) 'initial mol. frac. V1 = ',V1,' V2 = ', V2

```

```

C   Bulk Fugacity Calculation
    F1BULK=V1IN*P1*P
    F2BULK=V2IN*P2*P

```

```

    PETA=P
      Pold1=P
      Pold2=P
      Pold3=P
      Pold4=P
      WRITE(*,*)"BULK DONE"

```

```

C   Bulk calculations done

```

```

C-----Start iterating in ETA-----

```

```

C   Local slit calculations begin
C
C   ZETA: slit width in terms of a quantity of "fluid diameters"
C   DELETA: increment width in "fluid diameters" by which the
C   loop steps from the slit center to the edge of the region
C   able to hold complete particles
C   BETA: position in the slit relative to the edge of wall 1 in
C   terms of "fluid diameters";starts at center and works back
C   ETA: position in slit relative to wall 1 in terms of
C   "fluid-solid diameters"
C   XI: same as ETA except relative to wall 2

```

```

    INCREMENT=100
    BETA=ZETA/2.+(ZETA/2.-0.48)/INCREMENT
    DELETA=(ZETA/2.-0.48)/INCREMENT
    L=0
    WRITE (2,102)

```

```

WRITE(5,*)'DENB = ',DENB,' ',F1BULK = ',F1BULK
WRITE (5,*) 'Left to Right: BETA,ETA,L,DEN,P1,P2,F1,P,PSIA'
WRITE (5,*)

C BEGINNING OF STEP LOOP ACROSS SLIT
5 BETA=BETA-DELETA
ETA=(BETA*2.*SIGFF+SIGWW)/(SIGFF+SIGWW)
XI=(ZETA*SIGFF+SIGWW/2.-BETA*SIGFF)/SIGGS1
WRITE(12,*) 'L = ',L

FACTOR = 1.0

* SET DELTA P FOR PARTIAL DERIVATIVES (finite difference spec.)
DDP=.01*PETA

C Initial value of objective function for initial comparison
GOLD=1E5
C Counter variables (H is for fugacity matching loop)
K=0
H = 0

C Local calculation of attractive terms: Y1z and Y2z
C Reminder: Y1b and Y2b are bulk parameters
C Yz12: LOCAL intercomponent Y parameter
CALL YZCALC(BETA,Y1b,Y1z,ZETA)
CALL YZCALC(BETA,Y2b,Y2z,ZETA)
CALL YZCALC(BETA,Y12bs,Y12z,ZETA)

C Fluid-fluid fugacities for each component IN slit determined
C from 10-4 potential
F1 = F1BULK*EXP(PSIA(ETA)/T)
F2 = F2BULK*EXP(PSIB(ETA)/T)

C Pressure at a specific point inside the slit
C (Redefined from bulk pressure P)

C INITIAL PRESSURE GUESS FOR SLIT CENTER
P=F1/P1+F2/P2

C BEGINNING OF ITERATIONS ON V1, V2, AND P TO MATCH LOCAL
FUGACITY
C EXPRESSIONS; 200 STEPS MAX.

C 7 IF ((Pold1-Pold2) .GT. 3E5) THEN

```

```

C      DPDL1=(Pold1 - Pold2)
C      DPDL2=((Pold1-Pold2)-(Pold2-Pold3))/(Pold2-Pold3))
C      DPDL3=DPDL2-(((Pold2-Pold3)-(Pold3-Pold4))/(Pold3-Pold4))
C      P = Pold1 + FACTOR*DPDL1
C      ENDIF
C      IF (L .GT. 50) THEN
C        WRITE(2,*) 'P GUESS = ',P
C      ENDIF

C      WRITE(*,*) 'F1,F2,P',F1,F2,P

C      'bz' and 'cz' are designated local variables for b,c,q parameters
10     CALL BCQMIX(V1,V2,b1,b2,c1,c2,q1,q2,Y1z,Y2z,Y12z,bz,cz,qYbz,Ybz)

        IF (L .GT. 85) THEN
          WRITE(12,*) 'H = ',H
        ENDIF

C      Variables necessary for calculation of roots
        capBz=(bz*P)/(R*T)
        capqYBz=qYbz*P/R/T
        capYbz=Ybz*P/R/T

C      Calculate roots and type of case
        CALL SCUBIC(capBz,cz,Fsq,capqYBz,capYBz,R1,R2,R3,IFLAG)

C      Single root case
        IF(IFLAG.EQ.1) THEN
          Z1=R1
C      DENg is local density
          DENg=P/Z1/R/T
C      P1 and P2 are local fugacity coefficients redefined from bulk
          CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENg,V1,V2,q1,q2,qYbz,Ybz,
1          Z1,P1)
          CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENg,V2,V1,q2,q1,qYbz,Ybz,
1          Z1,P2)
*      CALCULATE OBJECTIVE FUNCTIONS (to match fugacity expressions)
          G1 = V1*P1*P/F1-1
          G2 = V2*P2*P/F2-1
          G3 = 1 - V1 - V2
          G0=SQRT(G1*G1+ G2*G2 + G3*G3)
          NROOT=1
          GOTO 25
        ENDIF

```

```

C   Double root case:
    IF(IFLAG.EQ.2) THEN
      Z1=R1
      Z2=R2
      IF(R2.GT.R1) THEN
        Z1=R2
        Z2=R1
      ENDIF
    ENDIF

C   Triple root case: take root yielding smallest initial objective
C   function
    IF(IFLAG.EQ.3) THEN
      CALL ARRANGE(R1,R2,R3)
      Z1=R1
      Z2=R3
    ENDIF

C   MULTIPLE ROOT FUGACITY ANALYSIS
C   Fugacity calculation for root 1 (Z1)--gas; DENg=gas density
      DENg=P/Z1/R/T
C   P1A AND P2A ARE LOCAL FUG. COEFF. FOR GAS ROOT
    CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENg,V1,V2,q1,q2,qYbz,Ybz,
1   Z1,P1A)
      CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENg,V2,V1,q2,q1,qYbz,Ybz,
1   Z1,P2A)

*   CALCULATE OBJECTIVE FUNCTIONS for gas phase
    G1A = V1*P1A*P/F1-1
    G2A = V2*P2A*P/F2-1
    G3A = 1 - V1 - V2
    G0A=SQRT(G1A*G1A+ G2A*G2A+ G3A*G3A)
C   WRITE(*,*)'G1A,G2A',G1A,G2A

C   UPPER ROOT TAKEN for 2 root case
    G0=G0A
    G1=G1A
    G2=G2A
    G3=G3A
    Z=Z1
    P1=P1A
    P2=P2A
    NROOT=1
      DEN=DENg

C   CRITERIA FOR DROPPING LOWER ROOT: WHEN (1-1.9*bz*DENI) < 0

```

C MEANING: REPULSIVE TERM BECOMES ATTRACTIVE DUE TO SIGN CHANGE

C (ALSO, LOWER ROOT FUGACITY DOESN'T NEED TO BE

C CALCULATED FOR 2-ROOT REGION)

DENI=P/Z2/R/T

IF((1-1.9\*bz\*DENI) .LT. 0) THEN

C PRINT\*, 'SKIPPING Z2'

GOTO 25

ENDIF

C Fugacity calculation for low root (Z2)--liquid; DENI=liq. density

C P1B AND P2B ARE FUG. COEFF. FOR LIQUID ROOT

CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENI,V1,V2,q1,q2,qYbz,Ybz,  
1 Z2,P1B)

CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENI,V2,V1,q2,q1,qYbz,Ybz,  
1 Z2,P2B)

\* CALCULATE OBJECTIVE FUNCTIONS for liquid phase

G1B = V1\*P1B\*P/F1-1

G2B = V2\*P2B\*P/F2-1

G3B = 1 - V1 - V2

G0B=SQRT(G1B\*G1B + G2B\*G2B + G3B\*G3B)

C WE TAKE THE ROOT THAT YIELDS AN INITIAL OBJECTIVE FUNCTION

C CLOSEST TO ZERO AS SHOWN BY NEXT STATEMENT; IT IS ASSUMED

C THAT THIS ROOT YIELDS THE 'CORRECT' FUGACITY REPRESENTATION

IN

C THE SLIT (APPLIES TO 3-ROOT REGION ONLY)

IF(G0A.GT.G0B) THEN

DEN=DENI

G0=G0B

G1=G1B

G2=G2B

G3=G3B

Z=Z2

P1=P1B

P2=P2B

NROOT=2

ENDIF

25 CONTINUE

PRINT\*, 'G0=',G0A,G0B, 'NROOT=',NROOT, 'IFG=',IFLAG

C Local Fugacity calc. wrt local composition and local pressure

F1CALC=V1\*P1\*P  
F2CALC=V2\*P2\*P  
VT=V1+V2

C WRITE(\*,\*) F1CALC,F1,P  
C WRITE(\*,\*) F2CALC,F2,H  
C PRINT\*, 'ETA,Y1',ETA,V2

C IF (IF K .LT. 1 .AND. GOLD.LT.G0) THEN  
C This block circumvents Newton-Raphson by using fractional  
C portions of the changes calculated from the previous  
C Newton-Raphson iteration.  
C K=K+1  
C V1=V1-DV1  
C V2=V2-DV2  
C P=P-DP  
C DV1 = DV1/2  
C DV2 = DV2/2  
C DP = DP/2  
C GOTO 100  
C END IF  
K=0  
GOLD=G0

9999 FORMAT(4G15.5,1X,I3)

IF (L .GT. 85) THEN  
WRITE(12,\*)'IFLAG = ',IFLAG,' NROOT = ',NROOT,' Z = ',Z  
WRITE(12,\*)' G0 = ',G0,' F1 = ',F1,' F2 = ',F2  
WRITE(12,\*)'P = ',P,' V1 = ',V1,' V2 = ',V2  
WRITE(12,\*)'G1 = ',G1,' G2 = ',G2,' G3 = ',G3  
WRITE(12,\*)  
ENDIF

C IF (P .GT. 1E8 .OR. (G0-GOLD) .GT. 1) THEN  
C FACTOR=FACTOR+0.1  
C IF (FACTOR .GT. 5) THEN  
C STOP  
C ENDIF  
C GOTO 7  
C ENDIF

C WHEN CONVERGENCE CRITERIA ARE MET, THIS BLOCK  
PROGRESSIVELY  
C INTEGRATES ADSORPTION OVER THE WIDTH OF THE SLIT  
IF(G0.LT.1E-3) THEN  
C WRITE (\*,\*) 'Bubble Pressure Calculation'

```

C  WRITE (*,101)
C  WRITE (*,103) X1,X2,T

      DEN=P/Z/8.314/T
      PETA=P
C  Component 1 local adsorption
      EXC1=SIGGS1*(V1*DEN-V1IN*DENB)*DELETA*1.E-4+EXC1
      AMT1=EXC1*Area/1000
C  AMT1=V1*DEN*SIGGS1*DELETA*Area*1.E-7+AMT1
C  Component 2 local adsorption
      EXC2=SIGGS1*(V2*DEN-V2IN*DENB)*DELETA*1.E-4+EXC2
      AMT2=EXC2*Area/1000
C  AMT2=V2*DEN*SIGGS1*DELETA*Area*1.E-7+AMT2

      WRITE (*,104) V1,DEN,P,BETA,H,L
      WRITE (2,104) V1,DEN,P,BETA,H,L,AMT1,AMT2
      WRITE (5,110) BETA,ETA,L,DEN,P1,P2,F1,P,PSIA(ETA)
101  FORMAT(10X,'X1',10X,'X2',10X,'T-K')
102  FORMAT(4X,'Y1',7X,'DEN',9X,'PRESS',9X,'ETA',8X,'H, L')
104  FORMAT(F8.5,2X,G12.5,2X,G12.5,2X,F5.3,2X,I4,2X,I4)
110  FORMAT(F5.1,1X,F5.1,1X,I3,1X,F7.3,
1     1X,F5.4,1X,F5.4,1X,G12.5,1X,G12.5,1X,G12.5)
      GO TO 200
      ENDIF

C  Incremental changes used in Newton-Raphson derivatives
      VV1 = V1 + DDV1
      VV2 = V2 + DDV2
      PP = P + DDP

*  CALCULATE DERIVATIVES WRT P
C  DENd: density in derivative variation
C  PN1,PN2: fug. coeff. in derivative variation

      capBz=(bz*PP)/(R*T)
      capqYBz=qYbz*PP/R/T
      capYBz=Ybz*PP/R/T
      CALL SCUBIC(capBz,cz,Fsq,capqYBz,capYBz,R1,R2,R3,IFLAG)

C  Single Root
      IF(IFLAG.EQ.1) THEN
          Z=R1
          DENd=PP/Z/R/T
          CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENd,V1,V2,q1,q2,qYbz,Ybz,
1  Z,PN1)
          CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENd,V2,V1,q2,q1,qYbz,Ybz,

```

```

1   Z,PN2)
    GOTO 30
ENDIF

```

```

C   Double Root: largest root always taken
IF(IFLAG.EQ.2) THEN
    BIG=R1
    SMALL=R2
    IF(R1.LT.R2) THEN
        BIG=R2
        SMALL=R1
    ENDIF
    R1=BIG
    R3=SMALL
ENDIF

```

```

C   Triple Root
IF(IFLAG.EQ.3) THEN
    CALL ARRANGE(R1,R2,R3)
ENDIF

```

```

IF(NROOT.EQ.1) THEN

```

```

C   If upper (gaseous) root was taken in original loc. calculation,
C   it will also be taken in this derivative calculation.

```

```

    Z=R1
    DENd=PP/Z/R/T
    CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENd,V1,V2,q1,q2,qYbz,Ybz,
1   Z,PN1)
    CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENd,V2,V1,q2,q1,qYbz,Ybz,
1   Z,PN2)
ELSE

```

```

C   If lower (liquid) root was taken in original calculation,
C   it will also be taken in this derivative calculation.

```

```

    Z=R3
    DENd=PP/Z/R/T
    CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENd,V1,V2,q1,q2,qYbz,Ybz,
1   Z,PN1)
    CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENd,V2,V1,q2,q1,qYbz,Ybz,
1   Z,PN2)
ENDIF

```

```

30  D1DP = (V1*PN1*PP-V1*P1*P)/DDP/F1
    D2DP = (V2*PN2*PP-V2*P2*P)/DDP/F2
    D3DP = 0

```

```

*   CALCULATE DERIVATIVES WRT V1

```

CALL BCQMIX(VV1,V2,b1,b2,c1,c2,q1,q2,Y1z,Y2z,Y12z,bz,cz,qYbz,Ybz)

capBz=(bz\*P)/(R\*T)

capqYBz=qYbz\*P/R/T

capYbz=Ybz\*P/R/T

CALL SCUBIC(capBz,cz,Fsq,capqYBz,capYBz,R1,R2,R3,IFLAG)

C Single root case

IF(IFLAG.EQ.1) THEN

Z=R1

DEND=P/Z/R/T

CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DEND,VV1,V2,q1,q2,qYbz,Ybz,

1 Z,PN1)

CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DEND,V2,VV1,q2,q1,qYbz,Ybz,

1 Z,PN2)

GOTO 40

ENDIF

C Double root case:

IF(IFLAG.EQ.2) THEN

BIG=R1

SMALL=R2

IF(R1.LT.R2) THEN

BIG=R2

SMALL=R1

ENDIF

R1=BIG

R3=SMALL

ENDIF

C Triple root case

IF(IFLAG.EQ.3) THEN

CALL ARRANGE(R1,R2,R3)

ENDIF

IF(NROOT.EQ.1) THEN

C If upper root was taken in original calculation, it will also

C be taken in this derivative calculation.

Z=R1

DEND=P/Z/R/T

CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DEND,VV1,V2,q1,q2,qYbz,Ybz,

1 Z,PN1)

CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DEND,V2,VV1,q2,q1,qYbz,Ybz,

1 Z,PN2)

ELSE

- C If lower root was taken in original calculation, it will also
- C be taken in this derivative calculation.

Z=R3

DEND=P/Z/R/T

CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DEND,VV1,V2,q1,q2,qYbz,Ybz,

1 Z,PN1)

CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DEND,V2,VV1,q2,q1,qYbz,Ybz,

1 Z,PN2)

ENDIF

40 D1D1 = (PN1\*VV1\*P-P1\*V1\*P)/DDV1/F1

D2D1 = (PN2\*V2\*P-P2\*V2\*P)/DDV1/F2

D3D1 = -1

- \* CALCULATE DERIVATIVES WRT V2

CALL BCQMIX(V1,VV2,b1,b2,c1,c2,q1,q2,Y1z,Y2z,Y12z,bz,cz,qYbz,Ybz)

capBz=bz\*P/(R\*T)

capqYBz=qYbz\*P/R/T

capYBz=Ybz\*P/R/T

CALL SCUBIC(capBz,cz,Fsq,capqYBz,capYBz,R1,R2,R3,IFLAG)

- \* Single root case

IF(IFLAG.EQ.1) THEN

Z=R1

DEND=P/Z/R/T

CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DEND,V1,VV2,q1,q2,qYbz,Ybz,

1 Z,PN1)

CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DEND,VV2,V1,q2,q1,qYbz,Ybz,

1 Z,PN2)

GOTO 50

ENDIF

- \* Double root case: largest root always taken

IF(IFLAG.EQ.2) THEN

BIG=R1

SMALL=R2

IF(R1.LT.R2) THEN

BIG=R2

SMALL=R1

ENDIF

R1=BIG

R3=SMALL

ENDIF

```

C   Triple root case
   IF(IFLAG.EQ.3) THEN
     CALL ARRANGE(R1,R2,R3)
   ENDIF

   IF(NROOT.EQ.1) THEN
C   Largest root is taken as in original calculation.
     Z=R1
     DENd=P/Z/R/T
     CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENd,V1,VV2,q1,q2,qYbz,Ybz,
1    Z,PN1)
     CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENd,VV2,V1,q2,q1,qYbz,Ybz,
1    Z,PN2)
   ELSE
C   Smallest root is taken as in original calculation.
     Z=R3
     DENd=P/Z/R/T
     CALL FUG(cz,c1,bz,b1,b2,Y1z,Y12z,DENd,V1,VV2,q1,q2,qYbz,Ybz,
1    Z,PN1)
     CALL FUG(cz,c2,bz,b2,b1,Y2z,Y12z,DENd,VV2,V1,q2,q1,qYbz,Ybz,
1    Z,PN2)
   ENDIF

50  D1D2 = (PN1*V1*P-P1*V1*P)/DDV2/F1
     D2D2 = (PN2*VV2*P-P2*V2*P)/DDV2/F2
     D3D2 = -1

*   CALCULATE INCREMENTS

     CALL INV(D1DP,D2DP,D3DP,D1D1,D2D1,D3D1,D1D2,D2D2,D3D2,DET)

     DV1 = -G1*D1D1 - G2*D1D2 - G3*D1DP
     DV2 = -G1*D2D1 - G2*D2D2 - G3*D2DP
     DP = -G1*D3D1 - G2*D3D2 - G3*D3DP
     PRINT*, ETA, V1, DV1, P, DP
     IF(ABS(DV1).GT.V1) THEN
       PRINT*, 'WARNING, LARGE DY', DV1
       DV1=0.5*V1*DV1/ABS(DV1)
       DV2=-DV1
C   P=9.E7
C   DP=0
     END IF
100 V1 = V1 + DV1
     V2 = V2 + DV2
     P = P + DP

```

```

IF (L .GT. 91) THEN
  WRITE(12,*) 'IFLAG = ',IFLAG,' NROOT = ',NROOT,' G0 = ',G0
  WRITE(12,*) 'Z = ',Z,' F1 = ',F1,' F2 = ',F2
  WRITE(12,*) 'P = ',P,' V1 = ',V1,' V2 = ',V2
  WRITE(12,*) 'G1 = ',G1,' G2 = ',G2,' G3 = ',G3
  WRITE(12,*)
ENDIF

IF(V1.LT.0)V1=0
IF(V1.GT.1)V1=1.
IF(V2.LT.0)V2=0
IF(V2.GT.1)V2=1.

H = H + 1

IF (H .LT. 200) GO TO 10
C  END OF ITERATIVE LOOP FOR MATCHING FUGACITY

PRINT*, 'ITERATIONS EXCEEDED'
  WRITE (12,*) 'ITERATIONS EXCEEDED'
C  DDV1=1E-3
C  DDV2=1E-3
C  DDP=.01*P
C  GOTO 10
200 CONTINUE
  L=L+1
C  Record previous 4 pressure values
  Pold4=Pold3
  Pold3=Pold2
  Pold2=Pold1
  Pold1=P
  IF(L.LT.INCREMENT+1) GOTO 5
C  END OF STEP LOOP ACROSS SLIT

WRITE(*,*) 'EXCESS1 = ',EXC1,' EXCESS2 = ',EXC2
  WRITE(*,*) 'AMT1 = ',AMT1,' AMT2 = ',AMT2
WRITE(2,*) 'EXCESS1 = ',EXC1,' EXCESS2 = ',EXC2
WRITE(2,*) 'AMT1 = ',AMT1,' AMT2 = ',AMT2

PRINT*, 'ENTER 1 FOR SAME T, DIFFERENT X1'
PRINT*, 'ENTER 2 FOR NEW T AND NEW X1'
PRINT*, 'ENTER 0 TO QUIT'
READ*, IDB
IF (IDB.EQ.1) GO TO 3

```

IF (IDB.EQ.2) GO TO 2  
END

\*\*\*\*\*

\* SUBROUTINES BELOW !!!!

\* EPSX: fluid-fluid interaction parameter  
SUBROUTINE YCALC(EPSX,T,Yij)  
Yij=exp(EPSX/T)-1.0617  
RETURN  
END

C-----  
SUBROUTINE BCQMIX(V1,V2,b1,b2,c1,c2,q1,q2,Y1,Y2,Y12,b,c,qYb,Yb)  
REAL V1,V2  
b=V1\*b1 + V2\*b2  
c=V1\*c1 + V2\*c2  
qYb=(V1\*\*2\*b1\*q1\*Y1+V1\*V2\*Y12\*(b1\*q2+b2\*q1)+V2\*\*2\*b2\*q2\*Y2)  
Yb=V1\*b1\*Y1+V2\*b2\*Y2  
RETURN  
END

C-----  
C This group of subroutines defines the coefficients in the  
C expression  $Z^{**3} + TM2*Z^{**2} + TM1*Z + TM0 = 0$   
SUBROUTINE TM2(B,Fsq,YB,T2)  
T2 = 1.7745\*YB-1-1.9\*B+Fsq  
\* WRITE (\*,\*) T2  
RETURN  
END

SUBROUTINE TM1(B,c,Fsq,YB,qYB,T1)  
T1 = -1.9\*1.7745\*B\*YB-1.7745\*YB+1.9\*B-4\*c\*B+9.5\*qYB+  
1 Fsq\*1.7745\*YB  
\* WRITE (\*,\*) T1  
RETURN  
END

SUBROUTINE TM0(B,c,YB,qYB,T0)  
T0 = 1.9\*1.7745\*B\*YB-4\*1.7745\*c\*B\*YB-9.5\*1.9\*B\*qYB  
\* WRITE(\*,\*) T0  
RETURN  
END

C-----  
C ESD Fugacity coefficient calculation for component i  
SUBROUTINE FUG(c,ci,b,bi,bj,Yi,Yij,rho,xi,xj,qi,qj,qYb,Yb,Z,PHI)

REAL lnPHI,PHI,TERM1,TERM2,TERM3a,TERM3b,TERM3c  
REAL TERM4a,TERM4b,TERM5

C WRITE(\*,\*)"IN FUG, CALCULATING TERM 1"

TERM1 = -(4./1.9)\*ci\*log(1-1.9\*b\*rho)

C WRITE(\*,\*)" TERM 1 DONE"

TERM2 = 4\*c\*bi\*rho/(1-(1.9\*b\*rho))

C WRITE(\*,\*)" TERM 2 DONE"

TERM3a = -(9.5/1.7745)\*log(1+1.7745\*Yb\*rho)/(Yb)

TERM3b = xj\*Yij\*(bi\*qj+bj\*qi)+xi\*Yi\*2\*bi\*qi

TERM3c = -qYb\*Yi\*bi/(Yb)

C WRITE(\*,\*)" TERM 3 DONE"

TERM4a = -(9.5\*qYb/(Yb))

TERM4b = Yi\*bi\*rho/(1+1.7745\*Yb\*rho)

C WRITE(\*,\*)" TERM 4 DONE"

TERM5 = -log(Z)

C WRITE(\*,\*)" TERM 5 DONE"

lnPHI =

TERM1+TERM2+TERM3a\*(TERM3b+TERM3c)+TERM4a\*TERM4b+TERM5

C WRITE(\*,\*)" SUMMATION DONE"

PHI = exp(lnPHI)

C WRITE(\*,\*)" PHI CALCULATED"

RETURN

END

C-----  
SUBROUTINE SCUBIC(B,c,Fsq,qYB, YB,R1,R2,R3,IFLAG)

CALL TM2(B,Fsq, YB, T2)

CALL TM1(B,c,Fsq, YB,qYB, T1)

CALL TM0(B,c, YB,qYB, T0)

\* WRITE (\*,\*) T2,T1,T0

CALL CUBIC(T2,T1,T0,R1,R2,R3,C1,C2,C3,IFLAG)

\* WRITE(\*,\*) IFLAG

\* WRITE(\*,\*) R1 R2 R3'

\* WRITE(\*,\*) R1,R2,R3

RETURN

END

C-----  
SUBROUTINE ARRANGE(R1,R2,R3)

C PROGRAM TO PUT 3 NUMBERS IN DESCENDING ORDER

DO 20 J=1,3

```
IF(R2.GT.R1) THEN
  TEMP=R1
  R1=R2
  R2=TEMP
ENDIF
```

```
IF(R3.GT.R2) THEN
  TEMP=R2
  R2=R3
  R3=TEMP
ENDIF
```

20 CONTINUE

```
RETURN
END
```

C-----

C 'YB' is bulk Y parm.; 'Y' is local Y parm.  
SUBROUTINE YZCALC(BETA,YB,Y,ZETA)

SA=ZETA-0.5-BETA

```
IF (BETA.LE.1.5) THEN
  BETAL=BETA
  SAL=SA
  IF(BETA.LT.0.5) THEN
    BETAL = 0.5
    SAL = ZETA - 1.0
  ENDIF
  Y1=BETAL+0.5
```

```
Y2=1.-1./SAL**3
Y3=1./3.*Y2
Y=YB*(Y1+Y3)*3./8.
END IF
```

```
IF(BETA.GT.(ZETA-1.5)) THEN
  Y1=SA+1.
  Y2=1.-1./(BETA-0.5)**3
  Y3=Y2/3.
  Y=YB*(Y1+Y3)*3./8.
END IF
```

```

IF((BETA.GT.1.5).AND.(BETA.LE.(ZETA-1.5))) THEN
  Y1=7./3.-1./3./(BETA-0.5)**3
  Y2=1.-1./SA**3
  Y3=Y2/3.
  Y=YB*(Y1+Y3)*3./8.
END IF

RETURN
END

```

C-----

```

SUBROUTINE
INV(D1DP,D2DP,D3DP,D1D1,D2D1,D3D1,D1D2,D2D2,D3D2,DET)
  CO11 = D2D2*D3DP-D3D2*D2DP
  CO12 = -(D2D1*D3DP-D2DP*D3D1)
  CO13 = D2D1*D3D2-D3D1*D2D2

  CO21 = -(D1D2*D3DP-D3D2*D1DP)
  CO22 = D1D1*D3DP-D3D1*D1DP
  CO23 = -(D1D1*D3D2-D3D1*D1D2)

  CO31 = D1D2*D2DP-D2D2*D1DP
  CO32 = -(D1D1*D2DP-D2D1*D1DP)
  CO33 = D1D1*D2D2-D2D1*D1D2

  DET = D1D1*CO11 + D1D2*CO12 + D1DP*CO13
*   WRITE(*,*) 'DET'
*   WRITE(*,*) DET
  D1D1 = CO11/DET
  D1D2 = CO21/DET
  D1DP = CO31/DET

  D2D1 = CO12/DET
  D2D2 = CO22/DET
  D2DP = CO32/DET

  D3D1 = CO13/DET
  D3D2 = CO23/DET
  D3DP = CO33/DET
RETURN
END

```

```

C   &7 1   2   3   4   5   6   7 2
C   *****
C   * SUBROUTINE CUBIC
C   *

```

```

C *****
C * THIS SUBROUTINE FINDS THE ROOTS OF A CUBIC EQUATION OF THE
*
C * FORM   X**3 + A2*X**2 + A1*X + A0 = 0   ANALYTICALLY.   *
C *****
C * VARIABLES
C *****
C * A0 ----- THE ZEROETH ORDER TERM OF THE NORMALIZED CUBIC
*
C *      EQUATION
C * A1 ----- THE FIRST ORDER TERM OF THE NORMALIZED CUBIC   *
C *      EQUATION
C * A2 ----- THE SECOND ORDER TERM OF THE NORMALIZED CUBIC   *
C *      EQUATION
C * C1 ----- THE COMPLEX ARGUMENT OF ROOT #1 OF THE EQUATION
*
C * C2 ----- THE COMPLEX ARGUMENT OF ROOT #2 OF THE EQUATION
*
C * C3 ----- THE COMPLEX ARGUMENT OF ROOT #3 OF THE EQUATION
*
C * CCHECK --- THE SAME AS "CHECK" BUT CONVERTED TO COMPLEX
*
C *      NUMBER FORMAT
C * CHECK --- Q**3 + R**2, USED TO CHECK FOR THE CASE OF THE   *
C *      SOLUTION AND IN FINDING THE ROOTS OF THE EQUATION, *
C *      DOUBLE PRECISION
C * DA0 ----- "A0" CONVERTED TO DOUBLE PRECISION
C * DA1 ----- "A1" CONVERTED TO DOUBLE PRECISION
C * DA2 ----- "A2" CONVERTED TO DOUBLE PRECISION
C * ES1 ----- AN INTERMEDIATE CALCULATION TO USED IN THE   *
C *      CALCULATION OF "S1"
C * ES2 ----- AN INTERMEDIATE CALCULATION TO USED IN THE   *
C *      CALCULATION OF "S2"
C * IFLAG ---- A FLAG TO INDICATE THE CASE OF THE SOLUTION OF THE
*
C *      EQUATION: =1 ONE REAL + TWO COMPLEX ROOTS,
C *      =2 ALL REAL ROOTS, AT LEAST TWO THE SAME
C *      =3 THREE DISTINCT REAL ROOTS
C * P1 ----- AN INTERMEDIATE SUM USED IN THE CALCULATION OF   *
C *      "SS1"
C * P2 ----- AN INTERMEDIATE SUM USED IN THE CALCULATION OF   *
C *      "SS2"
C * Q ----- AN INTERMEDIATE SUM USED IN CALCULATING "CHECK"
C * R ----- AN INTERMEDIATE SUM USED IN CALCULATING "CHECK"
C * R1 ----- THE REAL ARGUMENT OF ROOT #1 OF THE EQUATION
C * R2 ----- THE REAL ARGUMENT OF ROOT #2 OF THE EQUATION

```

```

C * R3 ----- THE REAL ARGUMENT OF ROOT #3 OF THE EQUATION *
C * RECK ---- THE SAME AS "CHECK", BUT SINGLE PRECISION REAL *
C * S1 ----- AN INTERMEDIATE VALUE USED TO FIND THE ROOTS OF *
C *           THE EQUATION, COMPLEX NUMBER *
C * S2 ----- AN INTERMEDIATE VALUE USED TO FIND THE ROOTS OF *
C *           THE EQUATION, COMPLEX NUMBER *
C * SS1 ----- THE SAME AS S1 BUT DOUBLE PRECISION REAL *
C * SS2 ----- THE SAME AS S2 BUT DOUBLE PRECISION REAL *
C * Z1 ----- ROOT #1 OF THE EQUATION, COMPLEX NUMBER *
C * Z2 ----- ROOT #2 OF THE EQUATION, COMPLEX NUMBER *
C * Z3 ----- ROOT #3 OF THE EQUATION, COMPLEX NUMBER *
C *****

```

```

SUBROUTINE CUBIC(A2,A1,A0,R1,R2,R3,C1,C2,C3,IFLAG)
  DOUBLE PRECISION CHECK,DA0,DA1,DA2,P1,P2,Q,R,SS1,SS2
  COMPLEX ES1,ES2,S1,S2,Z1,Z2,Z3,CHECK

```

```

  DA0 = DBLE(A0)

```

```

  DA1 = DBLE(A1)

```

```

  DA2 = DBLE(A2)

```

```

  Q = DA1/3.D00 - DA2*DA2/9.D00

```

```

  R = (DA1*DA2 - 3.D00*DA0)/6.D00 - (DA2/3.D00)**3

```

```

  CHECK = Q**3 + R*R

```

```

  IF (CHECK.GT.0.0) THEN

```

```

    IFLAG = 1

```

```

    P1 = R + DSQRT(CHECK)

```

```

    P2 = R - DSQRT(CHECK)

```

```

    IF (P1.LT.0.0) THEN

```

```

      SS1 = -DEXP((DLOG(-1.D00*P1))/3.D00)

```

```

    ELSE

```

```

      SS1 = DEXP((DLOG(P1))/3.D00)

```

```

    ENDIF

```

```

    IF (P2.LT.0.0) THEN

```

```

      SS2 = -DEXP((DLOG(-1.D00*P2))/3.D00)

```

```

    ELSE

```

```

      SS2 = DEXP((DLOG(P2))/3.D00)

```

```

    ENDIF

```

```

    R1 = SS1 + SS2 - DA2/3.D00

```

```

    R2 = -(SS1 + SS2) - DA2/3.D00

```

```

    R3 = R2

```

```

    C1 = 0.0

```

```

    C2 = (SQRT(3.))*(SS1 - SS2)/2.D00

```

```

    C3 = -C2

```

```

  ELSE IF (CHECK.LT.0.0) THEN

```

```

    IFLAG = 3

```

```

    RR = 1.*R

```

```

    RECK = 1.*CHECK

```

```

    CCHECK = CMPLX(RECK,0.0)

```

```

ES1 = CLOG(RR + CSQRT(CCHECK))/3.
ES2 = CLOG(RR - CSQRT(CCHECK))/3.
S1 = CEXP(ES1)
S2 = CEXP(ES2)
Z1 = (S1 + S2) - A2/3
Z2 = -(S1 + S2)/2 - A2/3 + (CMPLX(0.0,3**.5))*(S1 - S2)/2
Z3 = -(S1 + S2)/2 - A2/3 - (CMPLX(0.0,3**.5))*(S1 - S2)/2
R1 = REAL(Z1)
R2 = REAL(Z2)
R3 = REAL(Z3)
C1 = 0.0
C2 = C1
C3 = C1
ELSE
C *****
C * IF THE ROOTS OF THE EQUATION ARE VERY, VERY SMALL AND
VERY, *
C * VERY CLOSE TOGETHER, THIS SUBROUTINE MAY ERRONEOUSLY
REPORT *
C * THAT THE EQUATION HAS ONLY ONE ROOT NEAR ZERO *
C *****
IFLAG = 2
IF (R.LT.0.0) THEN
SS1 = -DEXP((DLOG(-1.D00*R))/3.D00)
ELSE IF (R.EQ.0.0) THEN
SS1 = 0.0
ELSE
SS1 = DEXP((DLOG(R))/3.D00)
ENDIF
SS2 = SS1
R1 = SS1 + SS2 - DA2/3.D00
R2 = -(SS1 + SS2)/2 - DA2/3.D00
R3 = R2
C1 = 0.0
C2 = C1
C3 = C2
ENDIF
RETURN
END
C &7 1 2 3 4 5 6 7 2

```

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