

## Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be “used for any purpose other than private study, scholarship, or research.” If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of “fair use” that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

**Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation**

Printing note: If you do not wish to print this page, then select “Pages from: first page # to: last page #” on the print dialog screen

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

## ABSTRACT

Title of Thesis: Thermodynamic and Leaching Studies of Various Systems

Satya Rami, Master of Science, 1988

Thesis directed by: Dr. Dana E. Knox

The group contribution approach is a reliable and fast method for the prediction of liquid phase activity coefficients in nonelectrolyte, nonpolymeric mixtures at low to moderate pressures and temperatures between 300 and 425 K. It has become widely used in practical chemical engineering applications in cases where little or no relevant experimental information is available.

The two group contribution methods examined in the course of this work, are the Knox and  $\xi$  UNIFAC models. Group interaction parameters are evaluated for each of these models and results compared. Although the results for both models are similar when sufficient data are available, the Knox model gives consistently better results with less data. (Reference 12).

Also studied during the course of this work was the Toxicity Characteristic Leaching Procedure, an EPA approved procedure for testing the Leaching Characteristics of contaminated soil.

THERMODYNAMIC AND LEACHING STUDIES  
OF VARIOUS SYSTEMS

By

Satya D. Rami

Thesis submitted to the faculty of the Graduate school of New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering, Dec 1988

Blank Page

APPROVAL SHEET

Title of Thesis : Thermodynamic and Leaching Studies of  
Various Systems

Name of Candidate: Satya D. Rami

Thesis and Abstract approved by: DANA E KNOX

Date: 1-12-89

Signature: [Signature]

Signature of other members of thesis committee:

Name: PIERO M ARMENANTE

Date: 1-12-89

Signature: [Signature]

Name: BASIL C. BALZIS

Date: 1-12-89

Signature: [Signature]

VITA

Name: Satya Rami

Permanent Address:

Degree and date to be conferred: Master Of Engineering  
Science, 1988

Date of birth:

Place of birth:

Secondary Education: O.L.P.S High School, April 1979

Collegiate Institutions attended	Dates	Degree	Date of degree
Indian Institute of Technology	1982-86	B.Tech	1986
New Jersey Institute of Technology	1986-88	M.S	1988

Major: Chemical Engineering

Positions held: Teaching Assistant

Department of Chemical Engineering

New Jersey Institute of Technology

Newark, NJ 07102

## **ACKNOWLEDGEMENT**

I would like to express my sincere appreciation and gratitude to Dr. Dana E. Knox , whose assistance and guidance has been instrumental to the success of this study.



## TABLE OF CONTENTS

	Page
LIST OF TABLES .....	ii
LIST OF FIGURES .....	ii
I. INTRODUCTION .....	1
II. THEORY OF GROUP CONTRIBUTION .....	5
UNIFAC Model	5
Knox Model	10
III. ACTIVITY COEFFICIENT .....	13
Qualitative Considerations	13
Vapor Liquid Equilibra	16
Experimental Determination of Activity Coefficient	17
IV. TOXICITY CHARACTERISTIC LEACHING PROCEDURE .....	19
Introduction	19
Methodology	19
Materials and Apparatus	20
Sample collection, Preservation and Handling	22
Procedure without Volatiles	22
Quality Assurance Requirements	29
V. Discussion of results	31
VI. Conclusion	34
V. References .....	48

## LIST OF TABLES

Table		Page
1	UNIFAC PARAMETERS	35
2	KNOX PARAMETERS	36
3	GROUP VOLUME AND SURFACE AREA PARAMETERS	37-40
4	VLE PREDICTION	41
4	TCLP RESULTS	42
5	TCLP VOLATILES	43

## LIST OF FIGURES

Figure		Page
1 2	AGITATION APPARATUS	44-45
3	ZHE - EXTRACTOR	46
4	TCLP FLOWCHART	47

## INTRODUCTION

Most common chemical engineering operations are separation processes. Many of these are diffusional operations of the phase-contacting type distillation, absorption, and extraction are probably the most common. For rational design of such separation processes, we require quantitative information on the phase equilibrium in the binary or multicomponent mixture under consideration. Since there exists a large variety of liquid mixtures in the chemical industry, the required experimental data are not always available. Hence it is essential that we correlate limited experimental data in such a way as to enable us to predict with confidence the activity coefficients of mixtures where little or no data are available.

The activity coefficient is a measure of phase nonideality. Relative to an ideal solution it is of considerable importance, especially in low pressure vapor liquid equilibria calculations. A correct understanding of the factors affecting it are essential for its complete grasp.

Activity coefficient is a function of:

- i) Concentration.
- ii) Molecular nature of the mixture components.
- iii) Temperature and Pressure.

There are two main models for the evaluation of activity coefficient.

\* The Wohl Type

\* The Local Composition type

Local composition models provide, typically, good correlation of binary vapor liquid equilibria data, which often are significantly better than those of a Wohl model. However they Local Composition method have several drawbacks, one of which being their ineffectivity when applied to multicomponent mixtures. This led to the development of the Group contribution approach.

Group contribution methods are often used for the estimation of physical properties and vapor liquid equilibria for compounds and mixtures. These models use the behavior of chemically similar systems to predict the properties of systems of interest. They do so by considering the fundamental units which compose a system not to be the molecules, but rather functional groups in the molecule. Thus intermolecular forces and energies are considered to be group-group interactions, and these can be characterized by study of chemically similar systems. Each molecule is considered as the sum of functional groups ( eg. nitro, amino, carboxyl....) which constitute a molecule. The thermodynamic properties are then correlated, not in terms of molecules, but rather in terms of functional groups which comprise the mixture.

The basic aim of the solution-of-group method is to utilise existing phase equilibrium data for predicting phase

equilibria of the systems for which no data are available. The method entails the following: suitable reduction of experimentally obtained activity coefficient data to obtain parameters characterizing interactions between pairs of structural groups in nonelectrolyte systems, and use of these parameters to predict activity coefficients for other systems which have not been studied experimentally, but contain the same functional groups. A group, is any convenient structural unit such as  $-\text{CH}_3$ ,  $-\text{COCH}_2-$  and  $-\text{CHCl}_2$ .

The two group contribution methods studied here are the Knox UNIFAC models. UNIFAC requires two group interaction parameters per group. However it was found ( 1 ) that these two parameters have a strong dependence on each other. Also single parameter expressions for the NRTL, LEMF, and UNIQUAC have been developed. Krummins et al ( 2 ) compared several of them and concluded that

- i) When all data are regressed, the single-parameter Wilson equation - with the ratio of molar volumes arbitrarily removed - gives the best results.
- ii) When only one infinite dilution activity coefficient is used, the single-parameter UNIQUAC equation gives best results.
- iii) Reliable results are up to fairly nonideal systems for Activity Coefficient  $< 10$ . Wong and Eckert ( 3 ) reached the same conclusion. The Knox model based on the group interaction approach and using one parameter is the first of its kind.

Toxicity Characteristic Leaching Procedure :

A major portion of this research project was to study the effect of different functional groups on the activity coefficient. Also conducted as a part of this research was a study of the the leaching properties of different elements found in contaminated soil. For this purpose the Toxicity Characteristic Leaching Procedure, which has been tested and approved by the EPA, was used.

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if it is disposed in a sanitary landfill, where decaying material would produce an acidic leachant. The TCLP is designed to determine the mobility of both organic and inorganic compounds present in liquid, solid and multiphase wastes.

Initially it was decided to carry out the TCLP and use the Knox model to verify the results. However, at the time of performing the experiments, soil samples containing organics were not available. Hence the leaching was conducted on soil samples obtained from packed bed columns to check for inorganics. An Induced Coupled Absorption Plasma (ICAP) then was used to analyse the samples. The detailed operating procedure and results are contained in the chapters 4 and 5 of this thesis.

## THEORY OF GROUP CONTRIBUTION METHODS

In this section we consider the theoretical basis of the UNIFAC and Knox models. We focus on their assumptions, advantages and shortcomings.

### UNIFAC Model

Origin: Estimation of thermodynamic properties of liquid mixtures from Group Contribution methods was first suggested by Langmuir [ 4 ]. This suggestion however, received little attention until Derr & coworkers [ 5, 6 ], used Group Contribution to correlate heats of mixing, following Wilson & Deal [ 7 ] who devised the solution of group method for activity coefficients. The UNIFAC method is based upon their ideas.

Aim: Like most other Group Contribution methods, UNIFAC aims to use the existing phase equilibra information to predict equilibra for systems where no such data exists. Though there are a large number of compounds in industry, they are made up of only a few fundamental structures, which are called functional groups. A group is any convenient structural unit such as  $-CH_3CN$ ,  $ACH$  etc.

Assumptions: UNIFAC is based on a few fundamental assumptions which are listed below.

i) The activity coefficient is assumed to be the sum of two contributions. They are the combinational part, essentially

due to the differences in size and shape of the molecule, and a residual part, essentially due to energy interactions.

For molecule  $i$  in any solution, this can be written mathematically as follows.

$$\ln \pi_L^{\text{TOTAL}} = \ln \pi_L^{\text{COMBINATORIAL}} + \ln \pi_L^{\text{RESIDUAL}} \quad \dots\dots\dots 1$$

The distinction between the two kinds of contributions to the activity coefficient is essential, since the liquid phase nonidealities caused by size and shape effects cannot be associated with group energetic interactions.

ii) The contribution from group interaction, the residual part, is assumed to be the sum of the individual contributions of each solute group in the solution, less the sum of the individual contributions in the pure component environment.

We write this as:

$$\ln \pi_L^{\text{R}} = \sum_{\text{all groups } k} V_k^{(i)} \left[ \ln \bar{T}_k - \ln \bar{T}_k^{(i)} \right] \quad \dots\dots\dots 2$$

$k=1,2,\dots,N$ , where  $N$  is the number of different groups in the mixture.

$\bar{T}_k$  is the residual activity coefficient of group  $k$  in a solution.  $\bar{T}_k^{(i)}$  is the residual activity coefficient of group  $k$  in a reference solution containing only molecules of type  $i$ , and  $V_k^{(i)}$  is the number of groups of kind  $k$  in molecule  $i$ .

iii) The individual group contributions in any environment containing groups of kinds  $1,2,\dots,N$  are assumed to be only a



function of group concentrations and temperature.

$$\overline{T}_K^{(i)} = F(X_1, X_2, \dots, X_n, T) \dots\dots\dots 3$$

The group fraction X is defined by

$$X_k = \frac{\sum_i v_k^{(i)} x_i}{\sum_j \sum_i v_j^{(i)} x_i} \dots\dots\dots 4$$

i = 1, 2, ..., M ( number of components )

j = 1, 2, ..., N ( number of groups )

According to this assumption, the residual activity coefficient for all mixtures of similar compounds may be calculated from the same function F. That is, the same parameters are used to represent the Vapor Liquid Equilibria in acetone - hexane and 5-nonanone - decane mixtures.

To formulate a special group contribution method for prediction of activity coefficients, one needs to specify:

- a) The equation used to calculate  $\ln \gamma_k^c$
- b) The equation used to calculate  $\tau_{kj}^c$
- c) Definition of functional groups used to build the molecules ( group assignment ).

The UNIFAC model is obtained by combining the UNIQUAC method with the solution of groups approach. The UNIFAC method is stated by equations 1 to 4.

Combinatorial activity coefficient for component i:

The combinatorial part of the activity coefficient in the UNIFAC model is given by the following equations:

$$\ln \tau_i^c = \ln \frac{\bar{\Phi}_i}{x_i} + \frac{z}{2} q_i \ln \frac{\bar{\Phi}_i}{\Phi_i} + l_i - \frac{\bar{\Phi}_i}{x_i} \sum_j x_j l_j \quad \dots 5$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1); \quad z = 10 \quad \dots 6$$

$$\bar{\Phi}_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad ; \quad \Phi_i = \frac{R_i x_i}{\sum_j R_j x_j} \quad \dots 7$$

Molecular surface  
area fraction

Molecular Volume  
fraction

$j=1,2,\dots,M$  ( number of components )

The Van der Waals volume:  $V_k$

and Van der Waals surface area:  $A_k$

$k=1,2,\dots,N$  ( number of groups in molecule i )

The constants representing group sizes and surface areas  $R_k$  and  $Q_k$  are obtained from atomic and molecular structure data, the Van der Waals group volumes and surface areas  $V_k$  and  $A_k$  (8):

$$R_k = V_k / 15.27$$

$$Q_k = A_k / (2.5 * 10^{**9})$$

The normalization factors 15.17 and  $2.5 * 10^{**9}$  are those derived by Abrams and Prausnitz ( 9 )

Residual activity coefficient for group k:

$$\ln \tau_k = Q_k \left[ 1 - \ln \left( \sum_m \Theta_m \Psi_{mk} \right) - \frac{\sum_m \Theta_m \Phi_{km}}{\sum_m \Theta_m \Psi_{km}} \right] \dots 8$$

m and n = 1,2...N ( all groups )

Equation ( 8 ) is similar to the one used in the UNIQUAC model for calculating

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad , \quad \Phi_m = \frac{\sum_j R_m^{(j)} X_j}{\sum_j \sum_l R_l^{(j)} X_j} \quad \dots\dots 9$$

Group surface area fraction  
 $j=1,2\dots M$  ;  $n=1,2\dots N$

Group fraction

A computer program which combined equations 1 to 9 was used to regress VLE data and determine interaction parameters. The procedure consisted of collecting VLE data for several binary systems. The only unknowns were two group-group interactions between two functional groups in each compound. VLE data was collected over a wide range of pressure and temperature, so that the group parameters evaluated had a wide range of applicability.

## KNOX MODEL

The Knox model is a one parameter Group-Contribution method. It uses only one energy parameter per group-group interaction. The development was accomplished theoretically rather than by reinterpreting the terms of a molecular model. Although the UNIFAC approach has been proved quite successful in a number of applications, there are still a number of drawbacks associated with the model. The most significant is the number of parameters. Very often the quantity of data available does not warrant the use of two parameters. Also the two parameters are found to be very strongly correlated. In addition we should note that the UNIFAC method represents an extension of the molecular-scale model UNIQUAC. This latter equation is based on the two-fluid concept which has been criticized by many authors (12). The KNOX model is a local Group-Contribution model which is not based on the two-fluid theory.

From the theoretical point of view, this model avoids the concept of hypothetical fluids while rigorously satisfying all material-balance constraints, thus suggesting a rational approach to the understanding of liquid mixtures from a molecular viewpoint.

## MODEL ASSUMPTIONS:

The basic assumptions of the KNOX model are:

1. The volume per molecule is unaffected by mixing ( no volume change of mixing ).

2. The number of groups of type k in a molecule of type i is given as  $v_{ik}$  and so the number of groups in the mixture,  $M_k$ , is given by:

$$M_k = \sum N_i v_{ik}$$

where  $N_i$  represents the number of molecules of type i.

3. The energies of molecular translation, rotation, and vibration are unaffected by mixing the energy change of mixing is thus determined solely by the numbers and types of interactions in the mixture.

4. The interactions in the mixture can all be characterized as group-group interactions, and that each type of interaction has a characteristic interaction energy which is independent of temperature, pressure and composition.

5. Each group of type k engages in a characteristic number  $Z_k$  of interactions with other groups.

The activity coefficient given by this model is as follows:

$$\ln \gamma_i = 1 - \frac{\Phi_i}{X_i} + \frac{Z_i}{2} \left( \frac{\Phi_i}{G_i} - 1 + \ln \frac{X_i}{\Phi_i} \right) \quad \dots\dots 10$$

$$(v = 1, 2, \dots, \infty)$$

$\bar{\phi}_i$  is the volume fraction and is given by:

$$\bar{\phi}_i = \frac{X_i v_i}{\sum_{j=1}^n X_j v_j} \quad (i = 1, 2, \dots, n) \quad \dots\dots 11$$

$\Theta_i$  is the molecular z-fraction and is given by:

$$\Theta_i = \frac{Z_i X_i / 2}{\sum_{j=1}^n Z_j X_j / 2} \quad (i = 1, 2, \dots, n) \quad \dots\dots 12$$

The most critical basic assumption on which this model is built is that a single energy parameter characterizes each molecular pair interaction. For pairs of molecules that exhibit specific interactions, such as hydrogen bonding, this assumption is invalid.

## ACTIVITY COEFFICIENT

The main objective of this section is to develop a qualitative and quantitative understanding of vapor liquid equilibrium which will assist us in developing a better understanding of Activity coefficient. The activity coefficient can be evaluated in several ways:

- a) Evaluation from experimental measurements.
- b) From its dependence on:
  - i) Concentration
  - ii) Molecular nature of the mixture components
  - iii) Temperature and Pressure

Frequently in industry, no experimental data are available for the systems under consideration. As it is not always feasible to carry out experiments to obtain this data, a theoretical model needs to be developed. For this reason many models involving the dependence of activity coefficient on Temperature, Pressure and liquid phase composition have been developed.

### QUALITATIVE CONSIDERATIONS:

Considering the importance of activity coefficient on VLE calculations - and the high cost of the experimental measurements required for their evaluation - a qualitative understanding of factors affecting it are helpful:

- a) Effect of Concentration: Consider a binary system of

molecules  $i$  in a large excess of molecules  $j$ . The molecules of component  $j$  are surrounded by their own, being oblivious of the existence of molecules of component  $i$ . Their activity coefficient is practically unity.

On the other hand molecules of component  $i$  are surrounded by molecules  $j$  and find themselves in a strange environment. Their activity coefficient is substantially different from unity, and this difference decreases with increase in number of molecules  $i$ .

b) Effect of molecular nature: Here we examine the effect of the molecular characteristics of the mixture component on its deviation from ideal solution behaviour. Consider a binary mixture where intramolecular ( $i-i$  and  $j-j$ ) forces are stronger than the intermolecular ( $i-j$ ) ones. As a result, the presence of component  $j$  increases the 'escaping tendency' of component  $i$ , as compared to its value at the same concentration, but in an ideal solution. The same is true for component  $j$ . Both activity coefficients are larger than one and this represents positive deviation from Raoult's law.

The differences in size and shape - especially size - between molecules  $i$  &  $j$  also affect the degree of nonideality. These effects are of entropic nature - and become dominant only when the ratio of molecular volumes is very large, such as in the case of solvent-polymer mixtures.



Typical values of gamma, positive deviations:

- \* completely miscible systems: 1-10
- \* partially miscible systems: 20-200
- \* very immiscible: 200-very high values.

For negative deviations, typical values for gamma are between 0.5 and 1.

c) Effect of Pressure Temperature:

The effect of pressure on the activity coefficient- at constant temperature and concentration - is given by:

$$\left[ \frac{\partial \ln \gamma_i}{\partial P} \right]_T = \frac{\bar{V}_i}{RT} \dots\dots\dots 13$$

where  $\bar{V}_i$  is the partial molar volume of component i in the liquid phase.

At conditions away from the critical point, we can replace, without any significant loss of accuracy,  $\bar{V}_i$  by  $V_i$  - the molar volume of pure liquid - and consider it independent of pressure. Integration, of 13 then leads to:

$$\frac{\ln \gamma_i(P_2)}{\gamma_i(P_1)} = \frac{V_i}{RT} (P_2 - P_1) \dots\dots\dots 14$$

It can be easily seen from the above equation that the effect of pressure on activity coefficient is small. (However the effect cannot be neglected at high temperatures and pressures).

Temperature:

The effect of temperature on the activity coefficient - at a constant pressure and concentration is given by:

$$\left[ \frac{\ln \gamma_i}{\delta T} \right]_{P, X} = \frac{-H_i^E}{R} \dots\dots\dots 15$$

The variation, thus, with temperature depends on the excess enthalpy of mixing, which reflects the difference between inter and intra-molecular forces. As a result the activity coefficient can be a strong function of temperature.

VAPOR-LIQUID EQUILIBRA:

Consider two phases, one liquid and one vapor, being in equilibrium with each other at some temperature ( T ) and Pressure (P).

The variables are:

- \* Liquid phase:  $X_1, X_2, \dots, X_{N-1} = N-1$
- \* Vapor phase :  $Y_1, Y_2, \dots, Y_{N-1} = N-1$
- \* (T) (P) : = 2
- \* total (NV) : = 2N

(where N is the number of components in the system.)

According to the phase rule: Degrees of freedom=  $N+2-2= N$

ie. For the complete specification of 2N variables, knowledge of N quantities is sufficient. Thus for a binary VLE system, knowledge of 2 variables suffices for a complete description of the intensive state of the system.

### EXPERIMENTATION DETERMINATION OF ACTIVITY COEFFICIENT:

We experimentally measure the vapor phase ( $y_i$ ) and the liquid phase ( $x_i$ ) composition of the mixture.

In case of vapor liquid equilibrium, we have equality of fugacities, ie.  $\bar{f}_i^v = \bar{f}_i^l$  .....16

a) Vapor phase fugacity is expressed through

$$\bar{f}_i^v = P y_i \hat{\Phi}_i \dots\dots\dots 17$$

The vapor phase fugacity coefficient can be evaluated with sufficient accuracy through an Equation of state.

b) The liquid phase fugacity is expressed through the Standard State approach.

$$\hat{f}_i^l = x_i \bar{f}_i^s = x_i \bar{f}_i^s \hat{\Phi}_i^s \left[ \exp\left(\frac{P - P_i^s}{R T}\right) \right] \dots\dots\dots 18$$

The fugacity coefficient of saturated pure liquid can be again evaluated from an Equation of state  $V_i$  is the molar volume of the same liquid, the exponential term is the Poynting correction. This is the low pressure or the Gamma Phi approach to VLE calculation.

$$\gamma_i = \frac{y_i P \hat{\Phi}_i}{x_i P_i^s \hat{\Phi}_i^s(P, T)} \dots\dots\dots 19$$

$P_i^s$ , the Vapor Pressure of the pure liquid can be calculated from some appropriate relationship, such as Antoine's equation.

To calculate fugacity coefficients we use the virial

equation. The fugacity coefficients of pure saturated liquids and of the components of vapor phase can be successfully evaluated through the virial equation, truncated to B.

$$\ln \bar{\phi}_i^L = \frac{B_{ii} P}{RT} \dots\dots\dots 20$$

$$\ln \bar{\phi}^V = \left( 2 \sum y_i B_{ij} - B \right) \frac{P}{RT} \dots\dots\dots 21$$

$B_{ii}$ ,  $B_{ij}$ ,  $B$  are second virial coefficients of the pairs  $i-i$ ,  $i-j$ , and mixture respectively. In the absence of experimental values second virial coefficients are predicted through Tsonoupoulas ( 10 ) or Hayden O' Connel ( 11 ) correlations which provide reliable estimates of B.

## Toxicity Characteristic Leaching Procedure (TCLP)

### I INTRODUCTION:

Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed off in a sanitary landfill. The TCLP is designed to determine the mobility of both organic and inorganic compounds present in liquid, solid and multiphase wastes.

### II METHODOLOGY:

1. For wastes containing less than 0.5% solids, the waste, after filtration through a 0.6-0.8 um glass fibre filter, was defined as the TCLP extract.

2. For wastes containing greater than 0.5% solids, the liquid phase, if any, was separated from the solid phase and stored for later analysis. The particle size of the solid was reduced (if necessary), weighed, and extracted with an amount of extraction fluid equal to 20 X the weight of the solid phase. Following the extraction the liquid extract was separated from the solid phase by a 0.6-0.8 um glass fibre filter filtration.

If compatible, the initial liquid phase of the waste was added to the liquid extract and analyzed following filtration. If incompatible, or if any volatiles were of concern, the liquids were analyzed separately and mathematically combined to yield a weighted average concentration.

## MATERIALS    APPARATUS

1. Agitation Apparatus: In carrying out this experiment an agitation apparatus which was capable of rotating the extraction vessel in an end over end fashion was used. A sketch of the agitation apparatus is depicted in figures 1 2

### 2.    Extraction Vessel:

Zero-Headspace Extraction Vessel (ZHE): In order to be acceptable when the waste was being tested for mobility of any of the compounds identified as being volatile, the extractor had to effectively preclude headspace. In addition to this, the Zero-Headspace extracting vessel also allowed for liquid/solid separation within the device, and was specifically designed to accommodate wastes which contained an initial liquid phase. This type of ZHE allowed for initial liquid/solid separation, extraction, and final extract filtration without having to open the vessel.

### Filtration Devices:

Zero-Headspace Extractor Vessel: When the waste contained an initial liquid phase and was being tested for any volatile compounds, the ZHE which allowed for liquid solid separation within the device was used. The device was capable of supporting and keeping in place a 0.6-0.8um glass fibre filter membrane and be able to withstand the pressure needed to accomplish separation ( 50 psi ). This type of ZHE vessel was

used to accomplish initial liquid/solid separation, extraction, and final extract filtration without having to open the vessel.

Reagents:

i Deionized distilled water: ASTM Type 2 deionized distilled water. Deionized distilled water was monitored periodically for impurities.

ii 0.1 N pH 5 Sodium Acetate Buffer: This media was made by adding the appropriate amount of Sodium acetate buffer solution (5N) to distilled deionized water to the appropriate volume (eg. by adding 50 ml of 5N sodium acetate buffer solution to distilled deionized water to a volume of 245 ml). This media was checked prior to use to insure that it met the above criteria. In addition, this media was checked frequently for impurities.

Soil Samples: In all six TCLP extracts were prepared. Two extracts of each of the following three soils were prepared.

- i) Residue from packed bed
- ii) Fly Ash sample
- iii) Contaminated soil from Bayonne water front

Analytical standards were prepared according to the appropriate analytical methods.

### Sample Collection, Preservation, and Handling

All samples must be collected using a sampling plan. Preservatives must not be added to the samples. Samples can be refrigerated unless it results in physical changes in the waste.

When the waste is to be evaluated for any constituents identified as being volatile on Table 6, care must be taken to see that the volatiles are not lost. When this is the case, samples must be taken and stored in such a manner which prevents the loss of volatile compounds. In addition, when volatiles are constituents of concern, if possible, any necessary particle size reduction must be accomplished by applying gentle force. (eg. squeezing or light hammer blows) to the waste particles through the tedlar bags such that they are reduced to the required particle size. Care is taken to insure that the tedlar bag is not punctured.

The TCLP extract was examined as soon as possible following the extraction. When storage was required the samples were stored at 4 C and samples for the volatiles were not allowed to come in contact with the atmosphere.

### Procedure when volatiles were not involved

NOTE: The general TCLP procedure when volatiles, as identified in Table 6, are not involved is essentially identical to the procedure when these constituents are involved. The only



difference is reflected in the need to insure that volatiles are not lost during the liquid/solid separation, extraction or analysis.

A minimum sample size of 10g is required, and larger size may be necessary depending on the percent solids in the waste sample. Enough waste sample was collected such that at least 5 grams of the solid phase of the waste (as determined using 0.6-0.8 um glass fibre filter filtration), was extracted. This insured that there is adequate extract for the required analysis.

\* If the waste was obviously dry, or would obviously yield no free liquid when subjected to 0.6-0.8 um glass fibre filter pressure filtration, a representative subsample of the waste (100 grams minimum) was weighed out to 0.1 grams accuracy. The TCLP extraction was then directly carried out.

\* If the sample was liquid or multiphasic, liquid/solid separation using 0.6-0.8 um glass fibre filter filtration was required.

\* The container which would receive the filtrate, was preweighed to 0.1 grams accuracy. Also preweighed were the filter membrane and prefilters.

\* The filter holder, membranes, and pre-filters were assembled.

\* A representative subsample of the waste was weighed to an

accuracy of 0.1 grams.

\* The sample was now evaluated for particle size. If the solid material had a surface area per gram of material equal to or greater than 3.4 sq cm, or was capable of passing through a 9.5 mm (0.375 inch) standard sieve, the extraction was immediately carried out.

If the surface area was smaller or the particle size is larger than described above, the solid material which did not meet the above criteria was separated from the liquid phase by sieving (or equivalent means), and the solid was prepared for extraction by crushing, cutting, or grinding to a surface area or particle size as described above. This particle size reduction was conducted under refrigeration. When surface area or particle size was appropriately altered, the solid was recombined with the rest of the waste.

NOTE: If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided if possible. If such exposure is unavoidable, the duration of the exposure must be kept to a minimum.

\* Waste slurries need not be allowed to stand to permit the solid phase to settle. Wastes that settle slowly may not be centrifuged prior to filtration. Since the Zero Head Extractor accomplished liquid/solid separation inside, prior settling or centrifugation of the waste was unnecessary.

\* The entire sample (liquid and solid phases) was transferred to the zero head extractor, and immediately inserted was the free moving piston in the Zero Head Extractor to the surface of the waste. The piston was secured against the sidewalls of the ZHE such that an air tight seal was formed. Care was taken not to secure the piston too tightly as this might cause damage to the filter.

NOTE: If the waste material has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the weight determined earlier, to determine the weight of the waste sample which will be filtered.

After securing the ZHE fittings tightly, the ZHE valve that allowed liquid to pass into the filtrate collection container was opened, and begin gentle pressure applied with the manual jack. This was continued until all liquid passed through the filter. In this method, the pressure was not applied directly to the waste. Rather, pressure was applied to the piston, which in turn, applied pressure to the waste for the required liquid/solid separation.

Filtration was stopped when all filterable liquid was separated from the waste. If this point was not reached under 10 psi, and if no additional liquid has passed through the filter in 5 minute interval, the pressure was slowly increased

in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 5 minute interval, proceeded to the next 10 psi increment. When liquid flow has ceased such that continuous pressure filtration at 50 psi did not result in additional filtrate within a 5 minute period, filtration was stopped. Pressure to the piston was discontinued, the Zero Head Extractor closed and the filtrate container disconnected.

\* The material in the ZHE is defined as solid phase of the waste, and the filtrate is defined as the liquid phase. If the original waste contains less than 0.5% solids, this filtrate is defined as the TCLP extract, and is analysed directly.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some materials which appears to be a liquid - but even after applying pressure filtration, this material will not filter. In this case, the material is carried through the TCLP extraction as a solid.

\* The weight of the liquid phase was measured upto 0.1 grams by subtracting the weight of the filtrate from the total weight of the filtrate filled container. The liquid phase was analysed as soon as possible. The weight of the liquid and soil phases was recorded.

\*\*\* The following are the details on how the appropriate amount of extraction fluid was added to the solid material within the ZHE and the agitation of the ZHE vessel.

\*\*\* The zero-headspace extraction vessel was placed in the rotary extractor apparatus, and checked to see that all fittings were secure.

A tube was connected from the source of fresh extraction fluid to the bottom of the ZHE valve (this was the same valve used to pass the initial liquid phase of the waste), and the valve slowly opened. The extraction fluid was allowed to flow slowly into the vessel while allowing the piston to move upwards, such that an amount of fresh extraction fluid equal to twenty times the weight of the solid phase of the waste was introduced into the ZHE vessel. After the extraction fluid was added to the ZHE vessel, the bottom ZHE valve was closed and removed from the tubing.

The ZHE was rechecked to ensure that all fittings were secure.

NOTE: As the extraction media contacts some wastes, gasses such as carbon dioxide may be formed within the ZHE vessel. Although some small bubbles may be present, if the above procedure is carefully followed, no headspace should appear within device.

\* The ZHE vessel was rotated at 28-32 rpm for 18 hours. The temperature was maintained between 20-25 C.

\* Following the 18 hour extraction, the material in the extractor vessel was once again separated into its component liquid and solid phases by filtering through the same 0.6-0.8 um glass fibre filter ( which was be examined to insure that it has remained intact).

NOTE: If the liquid material in the extractor is or appears to be multiphasic, the different phases should be filtered, collected and analyzed separately (if possible) , and the results combined.

NOTE: Only the samples of extract taken for volatiles analysis need be subject to the above filtration without exposure to the atmosphere. Samples of extract for other analysis (if any) should be handled with the same care as the volatiles sample, with the exception that the sample may be exposed to the atmosphere.

The ZHE is depicted in figures 1 & 2. This type of ZHE should be used when the waste is being evaluated for volatile compounds (See Table 6), and when the waste is not being evaluated for volatile compounds.

NOTE: If the waste contained an initial liquid phase, this liquid and the liquid extracted earlier are analysed separately, and the results are combined mathematically. If the extract is multiphasic, the individual phases can be analysed separately, and the results combined mathematically.

The following formula is used:

$$\text{Final Contaminant Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where

V = The volume of the phase (1)

C = The concentration of the contaminant of concern in the phase (mg/l)

The contaminant concentrations in the TCLP extract are compared to the appropriate regulatory thresholds.

#### Quality Assurance Requirements

- 1) All data, including quality assurance data, should be maintained and available for easy reference or inspection.
- 2) A minimum of one blank per five extractions was employed as a check to determine if contamination or any memory effects are occurring.
- 3) All extractions were performed in at least duplicate and the results averaged. When aliquots of the extract were filtered (as opposed to the entire extract) a minimum of two aliquots were analyzed and the results averaged.
- 4) All Quality Control measures described in the appropriate analytical methods was followed. The method of Standard addition was followed if:
  - i) Recovery of the compound from spiked distilled deionized water was not between 85 and 115 percent
  - ii) If the concentration of the constituent measured in the

extract was within 100% of the regulatory threshold level. (If more than one extraction is being run on samples of the same waste, the method of standard addition need only be applied once for every five extractions, and the percent recoveries applied to the remainder of the extractions.)

5) TCLP extracts were analyzed no later than 7 days after generation.



## DISCUSSION AND RESULTS:

Table 1,2 and 5 are results of the research of this thesis. Tables 1 and 2 are respectively the UNIFAC and KNOX group-group interaction parameters. Table 4 is a comparison of the results of the two models (Reference 12). It can be seen there is a large difference in average percentage errors when using UNIFAC values reported in literature and those actually evaluated using known VLE data. The reason for this is the larger database and wider temperature and pressure ranges that were used while evaluating the parameters found in literature. For the same data, with few exceptions, it can be seen that the KNOX parameters give clearly better results than the UNIFAC parameters. The parameter values for the Knox and UNIFAC parameters are consistent with those that were expected from theory. For stronger interactions we expect smaller values of interaction parameters. This is consistent with the value of  $-426.80$  for CH-CH<sub>2</sub> and a large value of  $527.92$  for ACH<sub>3</sub>-ACOH.

A computer program which combined equations 1 to 9 was used to regress VLE data and determine the interaction parameters. The procedure consisted of collecting VLE data for several binary groups. The only unknowns were two group-group interaction parameters between two of the functional groups in the compounds. VLE data was collected over a wide range of pressure and temperature, so that the parameters evaluated

have a wide range of applicability.

To cite an example of the procedure followed, let us consider the evaluation of the two interaction parameters for hydroxyl (-OH) and benzene (-ACH).

For this purpose four binary VLE systems containing the two groups were collected.

Binary System	Pressure Range mm Hg	Temperature 'C
Ethanol-Benzene	0 - 760	30
Propanol-Benzene	0 - 760	40
1-2 Butadiol-Benzene	0 - 760	25
Hexanol-Benzene	0 - 760	25

Ethanol ( $C_2H_5OH$ ), has one  $CH_3$ , one  $CH_2$ , and one OH group.

Benzene ( $C_6H_6$ ) has 6 ACH groups. The  $CH_3$ ,  $CH_2$ ,  $CH$ , and  $CH$  groups,

were first evaluated. The data for the four binary systems was then regressed using a computer program which incorporated equations 1 to 9 and the above data.

Table 5 consists of the TCLP results for the three different soil samples analyzed. The analysis was carried out on a Induced Couple Analytical Plasma (ICAP) at Chemtech, a certified analytical laboratory in Manhattan, New York. The instrument checked the presence and concentrations of twenty elements simultaneously and reported the average value of two experiments. When the concentration of an element was below the Instrument detection limit, the instrument reported

negative concentration values for that element.

The contaminated soil sample contained a high percentage of impurities and had to be diluted by a factor of 5 before analyzing it. Both experiments gave surprisingly similar concentration values, which proves the consistency of the TCLP method.

## CONCLUSION

The scope of this work involved a comparison of two Group Contribution models: The Knox and UNIFAC models. The purpose was to verify if the two UNIFAC parameters, which were found to be interdependent, could be replaced with one independent parameter (Knox model). Comparison of VLE results of each model shows that when the parameter(s) are evaluated from the same database the Knox model gives consistently better results. Also the Knox model requires a smaller database to provide reliable results. There was also found to be a large discrepancy between the values of UNIFAC VLE data published in literature and those evaluated in the scope of this work using a smaller database. This shows that for a smaller database UNIFAC lacks reliability while a one parameter model gives better results.

The TCLP method used to evaluate the leaching properties of soils gave consistent results, proving the reliability of the method.

## UNIFAC PARAMETERS

Table# 1

	CH	CH2	CH3	C	ACH	ACH3	OH	CH2N	CHNO2	CH=CH	CH2COO	CH3CN	ACOH
CH	0	-19.91	3000	0	-238.23	-108.41	31.22	54.06	300.22	43.74	607	722.9	1310.94
CH2	-49.98	0	602.23	0	-238.23	-108.41	31.22	54.06	300.22	43.74	607	722.9	1310.94
CH3	115.92	17.77	0	0	-238.23	-108.41	31.22	54.06	300.22	43.74	607	722.9	1310.94
C	0	0	0	0	-238.23	-108.41	31.22	54.06	300.22	43.74	607	722.9	1310.94
ACH	561.72	561.72	561.72	561.72	0	485.06	-34.38	111.33	91.82	256.38	563	445.46	1000
ACH3	177.17	177.17	177.17	177.17	-273.99	0	-370.51	-	X	X	203.31	3000	3000
OH	3000	3000	3000	3000	-11.64	-765.15	0	98.90	X	276.45	782.78	215.55	X
CH2N	188.07	188.07	188.07	188.07	-144.77	-	-568.74	0	-	-140.52	-	-	-
CHNO2	-68.06	-68.06	-68.06	-68.06	-70.08	X	X	-	0	X	-	-	-
CH=CH	86.74	86.74	86.74	86.74	-262.66	X	3000	3000	X	0	114.27	X	1149.11
CH2COO	-204.67	-204.67	-204.67	-204.67	-461.88	100.37	217.6	-	-	284.91	0	-57.16	X
CH3CN	34.34	34.34	34.34	34.34	-240.25	-213.81	36.21	-	-	X	-36.36	0	-
ACOH	1180.8	1180.8	1180.8	1180.8	2000	1313.92	X	-	-	-85.34	X	-	0

- PARAMETERS DO NOT EXIST  
X VLE DATA NOT FOUND IN LITERATURE

TABLE II

## Group Interaction Parameters: KNOX MODEL

Group	Group		Group	Group	
CH3	CH3	0.00	CH2	ACH	5.379
CH3	CH2	10.86	CH2	ACH3	20.26
CH3	CH	-426.80	CH2	OH	1242.00
CH3	C	812.40	CH2	CH2NH	41.61
CH2	CH2	0.00	CH2	CH2NO2	94.48
CH2	CH	-420.40	CH2	CH2=CH	27.04
CH2	C	563.30	CH2	CH2COO	62.35
CH	CH	0.00	CH2	CH3CN	85.32
CH	C	0.00	ACH	ACCH	1.57
OH	CH3CN	307.70	ACH3	CH2COO	118.42
ACH	CHNO2	58.02	ACH	OH	448.20
ACH	CH3CN	33.31	ACH3	OH	478.20
ACH	CH3COO	2.46	ACH	CH2N	-80.10
CH3CN	CH2COO	-39.43	ACH	ACOH	238.00
CH=CH2	CH3COO	40.31	CH2=CH	ACOH	86.22
CH2=CH	ACH	33.67	OH	CH2COO	139.39
CH2=CH	OH	-124.39	CH2N	CH2=CH	94.52
CH2	ACOH	349.60	ACH3	ACOH	527.92
CH3CN	ACH3	53.44			

Table 3 GROUP VOLUME AND SURFACE-AREA PARAMETERS

Main Group	Sub Group	No	$R_k$	$Q_k$	Sample Group Assignment
1 "CH <sub>2</sub> "	CH <sub>3</sub>	1	0.9011	0.848	Butane: 2 CH <sub>3</sub> , 2 CH <sub>2</sub> 2-Methylpropane: 3 CH <sub>3</sub> , 1 CH 2,2-Dimethylpropane: 4 CH <sub>3</sub> , 1 C
	CH <sub>2</sub>	2	0.6744	0.540	
	CH	3	0.4469	0.228	
	C	4	0.2195	0.000	
2 "C=C"	CH <sub>2</sub> =CH	5	1.3454	1.176	1-Hexene: 1 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CH <sub>2</sub> =CH 2-Hexene: 2 CH <sub>3</sub> , 2 CH <sub>2</sub> , 1 CH=CH 2-Methyl-2-butene: 3 CH <sub>3</sub> , 1 CH=C 2-Methyl-1-butene: 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> =C
	CH=CH	6	1.1167	0.867	
	CH=C	7	0.8886	0.676	
	CH <sub>2</sub> =C	8	1.1173	0.988	
3 "ACH"	ACH	9	0.5313	0.400	Benzene: 6 ACH Styrene: 1 CH <sub>2</sub> =CH, 5 ACH, 1 AC
	AC	10	0.3652	0.120	
4 "ACCH <sub>2</sub> "	ACCH <sub>3</sub>	11	1.2663	0.968	Toluene: 5 ACH, 1 ACCH <sub>3</sub> Ethylbenzene: 1 CH <sub>3</sub> , 1 ACH, 1 ACCH <sub>2</sub> Cumene: 2 CH <sub>3</sub> , 5 ACH, 1 ACCH
	ACCH <sub>2</sub>	12	1.0396	0.660	
	ACCH	13	0.8121	0.348	
5 "CCOH"	CH <sub>2</sub> CH <sub>2</sub> OH	14	1.8788	1.664	1-Propanol: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> CH <sub>2</sub> OH 2-Butanol: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CHOHCH <sub>3</sub> 3-Octanol: 2 CH <sub>3</sub> , 4 CH <sub>2</sub> , 1 CHOHCH <sub>2</sub>
	CHOHCH <sub>3</sub>	15	1.8780	1.660	
	CHOHCH <sub>2</sub>	16	1.6513	1.352	

Table 3 cont.

5 "CCOH"	CH <sub>3</sub> CH <sub>2</sub> OH	17	2.1055	1.972	Ethanol: 1 CH <sub>3</sub> CH <sub>2</sub> OH
	CHCH <sub>2</sub> OH	18	1.6513	1.352	2-Methyl-1-propanol: > CH <sub>3</sub> , 1 CHCH <sub>2</sub> OH
6	CH <sub>3</sub> OH	19	1.4311	1.432	Methanol: 1 CH <sub>3</sub> OH
7	H <sub>2</sub> O	20	0.92	1.40	Water: 1 H <sub>2</sub> O
8	ACOH	21	0.8952	0.680	Phenol: 5 ACH, 1 ACOH
9 "CH <sub>2</sub> CO"	CH <sub>3</sub> CO	22	1.6724	1.488	Ketone group is 2nd carbon; 2-Butanone: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>3</sub> CO
	CH <sub>2</sub> CO	23	1.4457	1.180	Ketone group is any other carbon; 3-Pentanone: 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> CO
10	CHO	24	0.9980	0.948	Acetaldehyde: 1 CH <sub>3</sub> , 1 CHO
11 "COOC"	CH <sub>3</sub> COO	25	1.9031	1.728	Butyl acetate: 1 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CH <sub>3</sub> COO
	CH <sub>2</sub> COO	26	1.6764	1.420	Butyl propanoate: 2 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CH <sub>2</sub> COO
12 "CH <sub>2</sub> O"	CH <sub>3</sub> O	27	1.1450	1.088	Dimethyl ether: 1 CH <sub>3</sub> , 1 CH <sub>3</sub> O
	CH <sub>2</sub> O	28	0.9183	0.780	Diethyl ether: 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> O
	CH-O	29	0.6908	0.468	Diisopropyl ether: 4 CH <sub>3</sub> , 1 CH, 1 CH-O
	FCH <sub>2</sub> O	30	0.9183	1.1	Tetrahydrofuran: 3 CH <sub>2</sub> , 1 FCH <sub>2</sub> O



Table 3 cont.

13 "CNH <sub>2</sub> "	CH <sub>3</sub> NH <sub>2</sub>	31	1.5959	1.544	Methylamine: 1 CH <sub>3</sub> NH <sub>2</sub> Propylamine: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> NH <sub>2</sub> Isopropylamine: 2 CH <sub>3</sub> , 1 CHNH <sub>2</sub>
	CH <sub>2</sub> NH <sub>2</sub>	32	1.3692	1.236	
	CHNH <sub>2</sub>	33	1.1417	0.924	
14 "CNH"	CH <sub>3</sub> NH	34	1.4337	1.244	Dimethylamine: 1 CH <sub>3</sub> , 1 CH <sub>3</sub> NH Diethylamine: 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> NH Diisopropylamine: 4 CH <sub>3</sub> , 1 CH, 1 CHNH
	CH <sub>2</sub> NH	35	1.2070	0.936	
	CHNH	36	0.9795	0.624	
15	ACNH <sub>2</sub>	37	1.0600	0.816	Aniline: 5 ACH, 1 ACNH <sub>2</sub>
16 "CCN"	CH <sub>3</sub> CN	38	1.8701	1.724	Acetonitrile: 1 CH <sub>3</sub> CN Propionitrile: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> CN
	CH <sub>2</sub> CN	39	1.6434	1.416	
17 "COOH"	COOH	40	1.3013	1.224	Acetic acid: 1 CH <sub>3</sub> , 1 COOH Formic acid: 1 HCOOH
	HCOOH	41	1.5280	1.532	
18 "CCl"	CH <sub>2</sub> Cl	42	1.4654	1.264	1-Chlorobutane: 1 CH <sub>3</sub> , 2 CH <sub>2</sub> , 1 CH <sub>2</sub> Cl 2-Chloropropane: 2 CH <sub>3</sub> , 1 CHCl 2-Chloro-2-methylpropane: 3 CH <sub>3</sub> , 1 CCl
	CHCl	43	1.2380	0.952	
	CCl	44	0.7910	0.724	
19 "CCl <sub>2</sub> "	CH <sub>2</sub> Cl <sub>2</sub>	45	2.2564	1.988	Dichloromethane: 1 CH <sub>2</sub> Cl <sub>2</sub> 1,1-Dichloroethane: 1 CH <sub>3</sub> , 1 CHCl <sub>2</sub> 2,2-Dichloropropane: 2 CH <sub>3</sub> , 1 CCl <sub>2</sub>
	CHCl <sub>2</sub>	46	2.0606	1.684	
	CCl <sub>2</sub>	47	1.8016	1.448	

Table 3 cont.

20 "CCl <sub>3</sub> "	CHCl <sub>3</sub>	48	2.8700	2.410	Chloroform: 1 CHCl <sub>3</sub> 1,1,1-Trichloroethane: 1 CH <sub>3</sub> , 1 CCl <sub>3</sub>
	CCl <sub>3</sub>	49	2.6401	2.184	
21	CCl <sub>4</sub>	50	3.3900	2.910	Tetrachloromethane: 1 CCl <sub>4</sub>
22	ACCl	51	1.1562	0.844	Chlorobenzene: 5 ACH, 1 ACCl
23 "CNO <sub>2</sub> "	CH <sub>3</sub> NO <sub>2</sub>	52	2.0086	1.868	Nitromethane: 1 CH <sub>3</sub> NO <sub>2</sub> 1-Nitropropane: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> NO <sub>2</sub> 2-Nitropropane: 2 CH <sub>3</sub> , 1 CHNO <sub>2</sub>
	CH <sub>2</sub> NO <sub>2</sub>	53	1.7818	1.560	
	CHNO <sub>2</sub>	54	1.5544	1.248	
24	ACNO <sub>2</sub>	55	1.4199	1.104	Nitrobenzene: 5 ACH, 1 ACNO <sub>2</sub>
25	CS <sub>2</sub>	56	2.057	1.65	Carbon disulfide: 1 CS <sub>2</sub>

Average Absolute Per Cent Errors Obtained in  
Prediction of Experimental Vapor Pressures of Mixtures.

System	°C	This Work	UNIFAC	UNIFAC(Lit)	Ref.
Pentane/Acetonitrile	60	8.91	3.39	2.30	11
Ethyl Acetate/Cyclohexane	20	5.21	44.75	8.16	12
Ethyl Acetate/Pentyl Acetate	20	4.71	5.33	5.72	13
Methyl Acetate/Pentyl Acetate	40	2.49	9.00	2.35	14
Methyl Acetate/Propyl Acetate	40	2.46	6.92	2.49	14
1-Hexene/n-Hexane/n-Octane	55	4.85	0.90	0.71	15
1-Heptene/n-Heptane/n-Octane	55	2.02	4.17	4.22	16
1-Pentene/n-Pentane	20	0.25	2.05	2.72	17
n-Pentane/Cyclohexene	20	1.41	15.67	3.76	17
Methylamine/n-Butane	15	5.19	11.96	2.53	18
Methylamine/n-Nonane	20	24.78	37.06	5.44	18
Ethylamine/Triethylamine	0	6.83	10.12	9.38	19
Diethylamine/Triethylamine	20	2/16	2.46	0.50	19
Cyclohexane/1-Propanol	25	21.07	9.80	3.71	20
Ethanol/3-Methylbutanol	50	2.32	6.11	4.48	21
1-Propanol/2-Methyl-1-propanol	60	0.47	1.20	0.25	22
n-Pentane/Ethanol	20	181.50	34.49	2.96	23
Benzene/n-Octane	55	6.04	5.21	0.12	24
Benzene/Cyclohexane	40	2.32	3.75	0.59	25
Benzene/n-Tetradecane	40	2.18	6.93	0.49	26
Benzene/n-Heptadecane	40	0.87	4.04	1.36	26
Benzene/2,2,4-Trimethylpentane	25	11.47	7.83	6.24	27
Benzene/Toluene	10	1.15	0.85	1.56	13
Benzene/m-Xylene	37	1.37	2.40	4.12	28
Benzene/Toluene	40	3.43	2.80	4.42	13
Cyclohexane/Toluene	20	1.27	2.95	2.56	29
3-Methylpentane/Toluene	30	5.35	8.32	2.43	30
n-Heptane/Toluene	40	3.88	7.45	0.59	31
3-Methylpentane/Toluene	50	5.75	7.67	1.91	30
Cyclohexane/1-Nitropropane	45	7.24	4.49	4.45	32
Methylcyclohexane/Nitroethane	45	4.21	14.86	1.80	33
n-Hexane/Nitroethane	45	3.89	23.64	8.22	34
n-Octane/2,2,4-Trimethylpentane/Nitroethane	35	9.85	22.66	3.45	34
n-Octane/Nitroethane	35	7.44	26.20	4.24	34

From Reference# 12

TABLE 5

## TCLP EXTRACT RESULTS

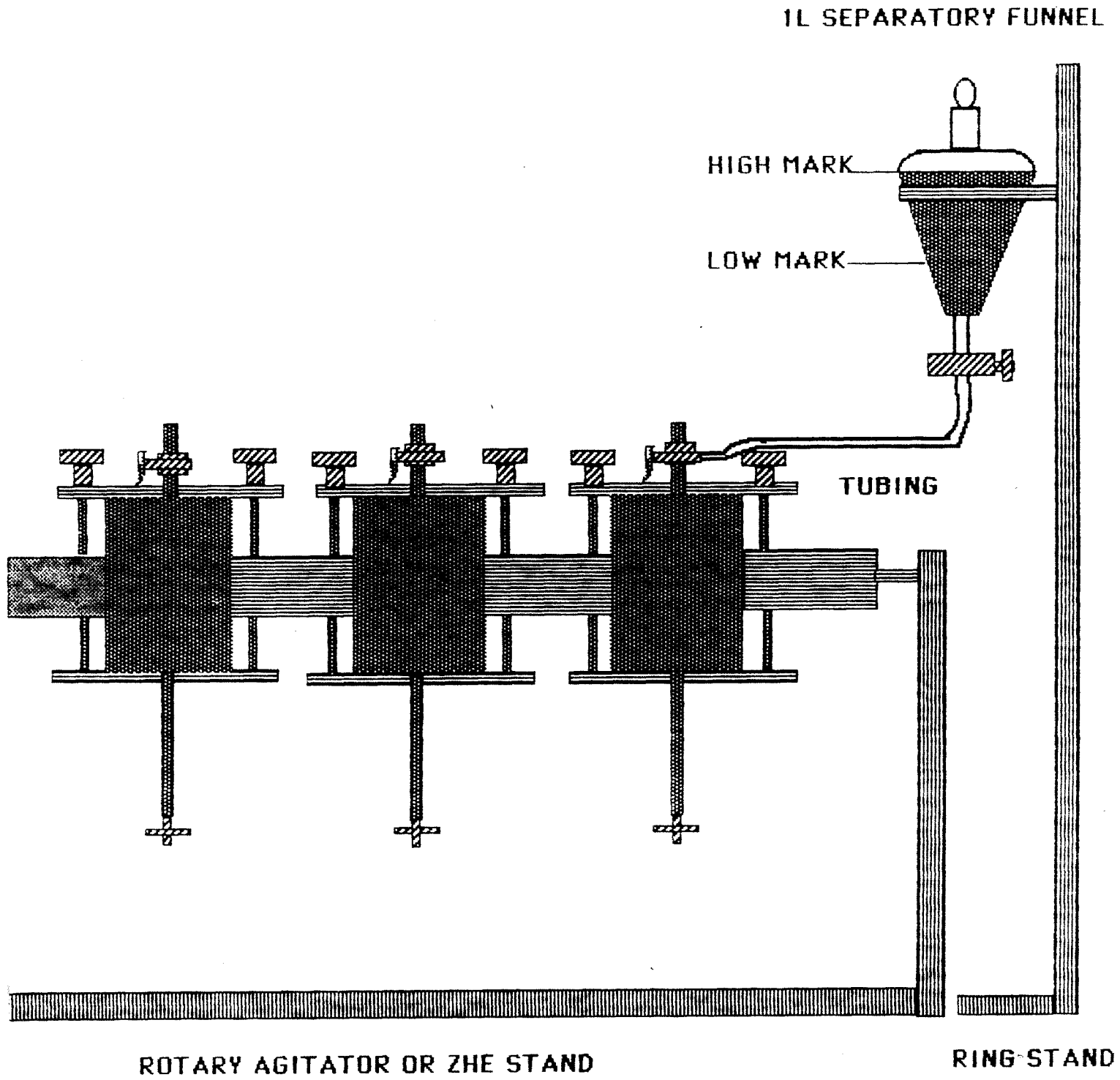
Instrument: ICAP  
Units: mg/L

Element	Packed bed Residue	Fly Ash sample	Contaminated soil
Al	262.00	0.347	0.048
As	2.46	0.06	0.096
Ba	7.98	0.55	0.60
Be	0.04	-	-
Cd	0.08	0.07	0.075
Ca	358.80	4753.00	4575.00
Cr	17.53	0.022	0.025
Co	0.34	0.008	0.012
Cu	0.73	0.24	0.25
Fe	202.90	0.13	0.24
Pb	-	0.62	0.16
Mg	23.10	232.70	255.00
Mn	5.33	7.96	1.87
Ni	14.74	0.29	3.50
Na	63.68	21.49	16.20
Zn	20.56	0.41	0.45

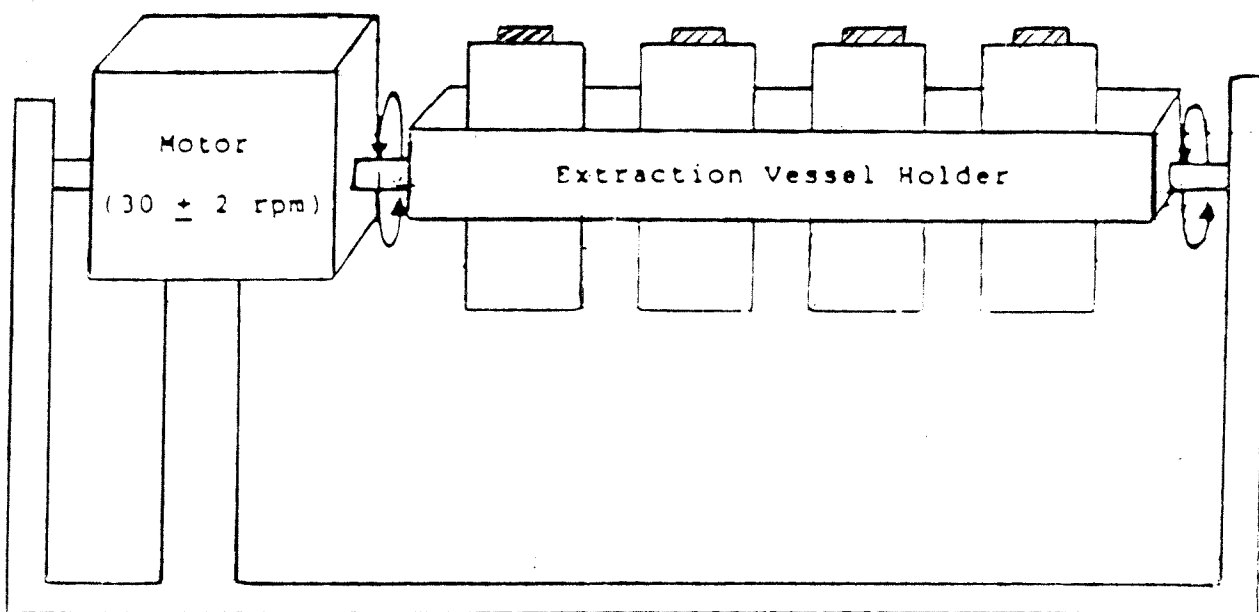
TABLE 6  
VOLATILE CONTAMINANTS

ACETONE  
N-BUTYL ACHOHOL  
CARBON BISULFIDE  
CARBON TETRACHLORIDE  
CHLOROBENZENE  
METHYLENE CHLORIDE  
METHYL ETHYL KETONE  
METHYL ISOBUTYL KETONE  
TETRACHLOROETHYLENE  
TOLUENE  
1,1,1 - TRICHLOROETHANE  
TRICHLOROETHYLENE  
TRICHLOROFLUOROMETHANE  
XYLENE

FIGURE# 1



FIGURE# 2



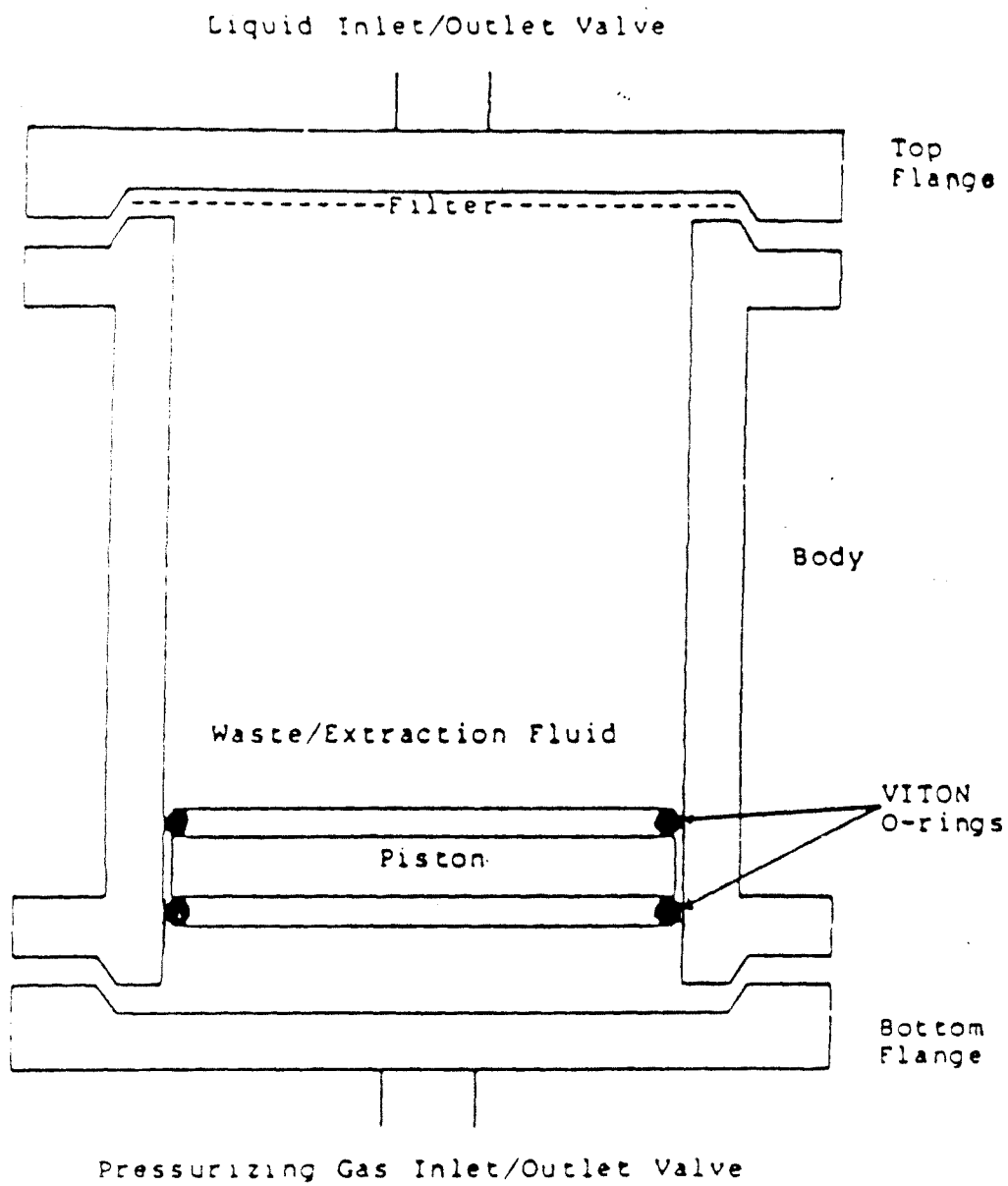
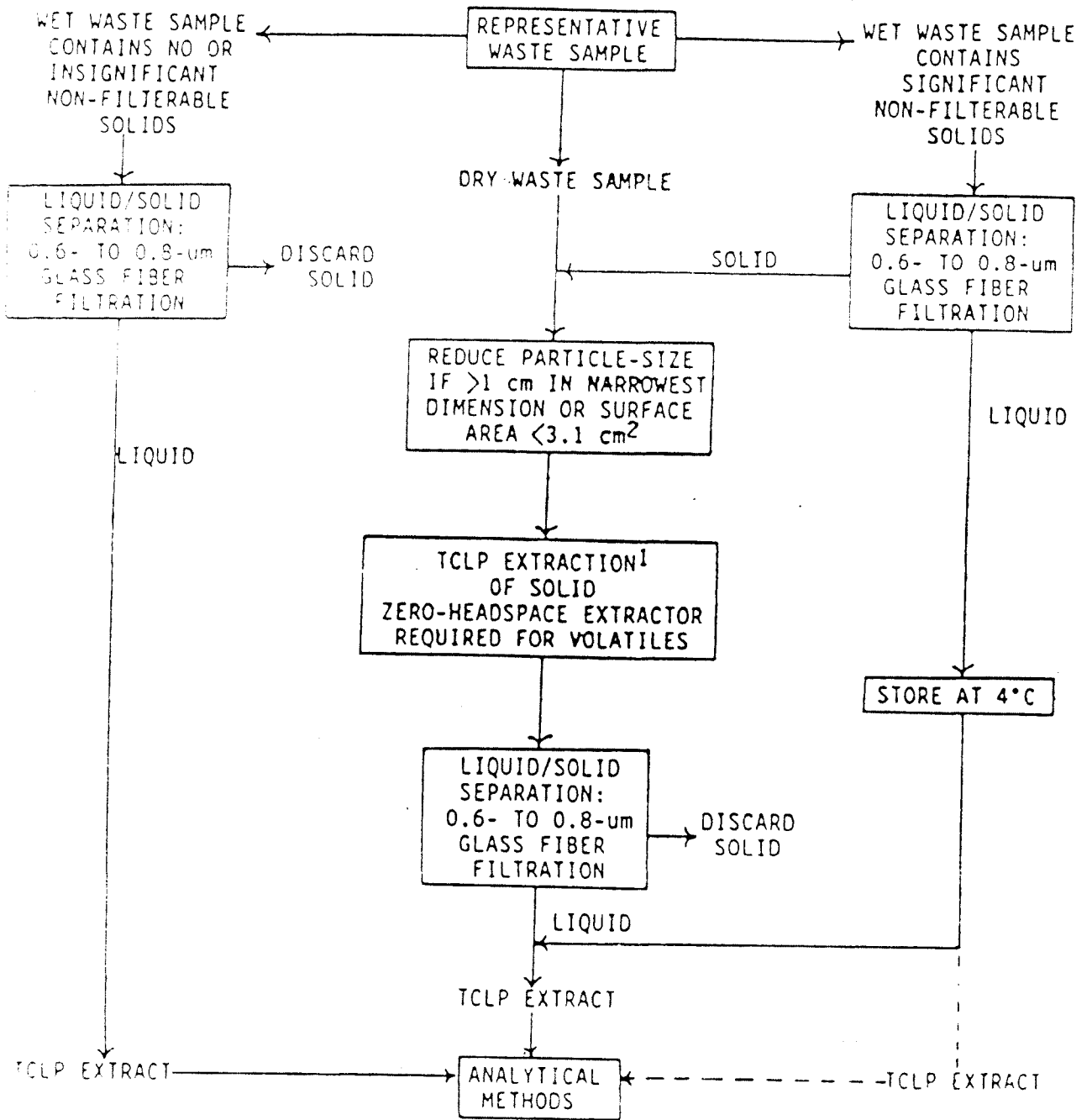


Figure 3: Zero-Headspace Extraction Vessel





¹The extraction fluid employed is a function of the alkalinity of the solid phase of the waste.

FIGURE 4: TCLP FLOWCHART

## REFERENCES

1. Hakinson, R., Laugfitt, B., Tassios, T.  
Can. J. Chem Eng., 1972, 50, 571
2. Krummins, A., Rastogi, A., Russac, M., Tassios, T.  
Can. J. Chem. Eng., 1980, 58, 663
3. Wong, K., Eckert, C.  
Ind. Eng. Chem. Fund., 1971, 10, 1
4. I. Langmuir, The Distribution and Orientation of  
Molecules, Third Colloid Symposium Monograph, The  
Chemical Catalog Co. Inc., NY 1925
5. O. Redlich, E.L. Derr G. Pierotti  
J. Am. Chem. Fund. 81 (1959), 2283
6. E.L. Derr M. Papadopoulos  
J. Am. Chem. Fund. 81 (1959), 2285
7. G.M. Wilson C.H. Deal  
Ind. Eng. Chem. Fund, 1 (1962), 20
8. A. Bond, Physical Properties of Molecular Crystals,  
Liquids and Glasses, Wiley, NY, 1968.
9. D.S. Abrahams J.M. Prausnitz  
A. I. ChE Journal, 21 (1975) 116
10. Tsonoupoulas. Adv in Chem. Ser. 115., Am Chem Soc.  
(1972) 46.
11. J.D. Hayden & J.P. O'Connell, Ind. Eng. Chem. Pros. Des.  
Dev. 14 (1975) 209.
12. Dr. Dana E. Knox, J. Soln. Chem., vol 6, No 8, 1987  
One Parameter Group Contribution Model
13. Model for representation of  $G^E$   $H^E$   
Dana E. Knox and H.C. Van Ness  
Fluid Phase Eq, 15 (1984) 267-285
14. Test Methods for evaluating Solid Wastes  
Vol IC, Lab Manual, Phy/Chem methods
15. Hazardous Waste Management System  
40 CFR Part 260 et seq, EPA Part II
16. A. Fredenslund, J. Gmehling  
Vapor-Liquid Equilibra  
E.N.H. Inc., (1977)