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# AMINE REMOVAL FROM AQUEOUS PROCESS STREAMS BY LIGAND EXCHANGE

### A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemical Engineering

by Wayne Bernard Bolden B.S., University of Tennessee, 1982 M.S., Louisiana State University, 1984 December, 1986

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#### ABSTRACT

Amines in aqueous, process feed or effluent streams can cause contamination problems. Ligand exchange demonstrates the potential to remove amines from these process streams. In ligand exchange, a complexing solute is removed from solution as it covalently bonds to a metal ion held on has Previous work cation exchange resin. shown copper(II)-carboxylic acid resin to be а suitable metal-resin exchange sorbent. The results of a research program are presented showing the applicability of ligand exchange to an amine removal operation. This study includes experimental determination of equilibrium relationships and diffusion coefficients. These parameters have been used to mathematically model ligand sorption in fixed-bed columns.

Considerable attention has been given to mathematical prediction of ligand exchange. Analytical and numerical solutions were used to describe batch sorption and exchange column performance. Numerical solutions were required to fundamentally account for the nonlinear sorbent-liquid equilibrium. An experimental program was conducted for two amines, butylamine and diglycolamine. The corresponding ligand-sorption processes were found to be mass-transfer controlled with pore diffusion as the dominating mechanism.

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Predictions of ligand-sorption column profiles encourage extensions to multicomponent ligand exchange and allow design for full-scale applications.

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#### Chapter I

#### INTRODUCTION

Amination by ammonolysis, the process of forming amines by the reaction of ammonia with organic groups, is an important process in the synthetic chemical industry of the United States [1]. The worldwide production of fatty amines and their derivatives was approximately 300,000 tons in 1982 [2]. Commercial production of primary amines is based on catalytic hydrogenation of nitriles using heterogeneous catalysis. Secondary amines are produced from nitriles, primary amines, fatty alcohols or a mixture thereof. Tertiary amines are manufactured by reductive alkylation of primary and secondary amines with formaldehyde, or reacting long-chain alcohols or alkyl halides with other amines.

Fugitive amine emissions can cause contamination problems in wastewater and process water streams. First, the alkyl derivatives of some amines can form carcinogenic nitrosamines [1]. Second, they can indirectly contribute to oxygen depletion in receiving streams via the biological nitrogen cycle. Finally, amines tend to plate out on heat exchanger tubes and reduce their effectiveness [3].

# 1.1 Ligand Exchange

Ligand exchange is a process in which amines and other complexing substances are removed from aqueous solutions. A ligand, an ion or a polar molecule, is a Lewis base. It donates a pair of electrons that functions as a coordinate covalent bond between itself and the central ion. Ligands are stripped from the solution phase by complexing with a metal ion held on an ion exchange resin. This complexation occurs within the metal-resin matrix. The chemisorbed ligands replace either solvent molecules or other ligands in previously formed complexes to occupy the metal-ion coordinative valences. Ideally, no ion exchange takes place and the ion exchange resin functions only as a solid support the complexing metal ion [4]. This for research investigates the use of copper(II)-carboxylic acid resin as an appropriate ligand-exchanging sorbent. The chemistry of a typical exchange reaction is shown in Figure 1 as a primary amine replaces the solvation shell of copper on carboxylic acid resin. This process has the advantages of increased resin capacity over conventional ion exchange and selective removal of amines from solutions containing non-complexing compounds.







Figure\_1: The Chemistry of Ligand Exchange

# 1.2 Industrial Amine Pollution

Alphatic amines are used widely in industry for solvent extraction [5,6] and acid gas removal [7-10].

# <u>1.2.1</u> Solvent Extraction

A new sludge-treatment process has been reported that uses triethylamine as a dewatering agent [5]. The process separates viscous oily waste into three fractions: oil for use as ship fuel, water that needs further treatment before discharge and oil-free dry solids to be contained at the The triethylamine solvent is added to proposed plant site. the sludge, absorbing oil and much of the water. The resulting cake is dewatered by vacuum filter, press or centrifuge and dried at 250-290°F. Amine solvent and water vapors are condensed and combined with liquid from the dewatering step. This mixture is heated and collected in a decanter, where the water and triethylamine separate. The amine solvent is then distilled to remove oil from the bottoms and recycled to mix with fresh sludge. Even though a much higher heat of vaporization than water has triethylamine (1000 versus 133 Btu/lb), some of the amine will invariably be distributed to the water phase. Thus, the effluent water will require treatment for amine removal.

Tertiary amines have been used to extract metals from aqueous solutions for more than 20 years [6]. The chemistry of amine extraction offers good potential for future growth in the metals industry. The solvent extraction process

typically consists of two sections of mixer-settler stages. In the extraction section, the amine in a water-immiscible organic solvent (normally kerosene) contacts an aqueous solution of the metal to be extracted in the mixer. The dispersion passes to the settler and the phases separate. The aqueous solution leaving the extraction section is referred to as the raffinate. The organic phase containing the metal values (called the loaded organic) is then transferred to the stripping section, where the metal values are stripped from the organic phase to an aqueous solution for subsequent treatment. The stripped organic liquor is recycled back to the extraction section. The effectiveness of this operation involves repeatedly contacting the organic with large volumes of aqueous phase. So, amine losses due to solubility in the aqueous phase must remain low. This process is economically marginal when the constant solubility losses are greater than 50 ppm.

# 1.2.2 Acid Gas Treating

The most common impurities in natural gas, oil refinery or petrochemical plant gases are acid-forming gases such as  $H_2S$ and  $CO_2$  [10]. Scrubbing these gases to remove the acid components is a basic step minimizing environmental pollution. Acid gas must be scrubbed because of the toxicity of  $H_2S$ , the corrosiveness of  $CO_2$  and  $H_2S$  in wet gas streams, and the lack of heating value of  $CO_2$  [12]. Alkanolamines, or alkyl alcohol amines, have been

successfully used to treat sour (sulfur-containing) gas for  $H_2S$  and  $CO_2$  removal for over 30 years. More recently, alkanolamines have also been used to purify flue gas, liquid hydrocarbon streams and process gas streams.  $H_2S$  and  $CO_2$  are acid gases because they dissociate in an aqueous medium to form a weak acid. The amines are weak organic bases. An acid gas and an amine base combine chemically to form an acid-base complex (salt) in solution.

Primary amines are chemically stronger bases than secondary amines, hence they are more reactive towards  $H_2S$ and  $CO_2$  and will form a stronger bond with the acid gases. The bond strength is directly related to the equilibrium characteristics of the amines. This knowledge has been the basis of many proprietary amine solvents for acid gas scrubbing. Dow Chemical Co. uses a special amine solvent for its new  $CO_2$  recovery process [13]. Another relatively new solvent is BASF's methyldiethanolamine, which began production in late 1982 and mid-1984 [14]. In mid-1985, Union Carbide Corp. introduced two alkanolamines for  $CO_2$ removal; Amine Guard Solvent N-1 and UCARSOL CR Solvent 401 [14].

Selectivity in acid gas treatment can be directly related to the molecular structure of the amine. Exxon Research and Engineering Co. recently developed a series of amine gas treating agents called FLEXSORB [15,16]. They found that bulky groups attached to the amine nitrogen cause steric

crowding which blocks the nitrogen-carbon bond to  $CO_{g}$ . However, these molecular structures do not impede the reaction of the smaller hydrogen atom of  $H_{g}S$  with the amino group nitrogen. Amines with this arrangement are called "hindered" amines. They are usually primary or secondary amines in which at least one "voluminous" group, generally an alkyl one, replaces the hydrogen bound to a carbon near the amine nitrogen [17]. Control of the molecular substituent groups allows tailoring of amines for specific treating functions.

In acid gas treating operations, an amine solution contacts a gas stream, reacts with the acid gas impurities and chemically absorbs them. The amine solution can then be treated with steam (thermal regeneration) to decompose the salt and strip out the  $H_2S$  and  $CO_2$ . The regenerated amine solution is then recycled to clean up more gas. Amines are lost in this operation to process wastewater by direct discharge from the amine regeneration system and drainage from the fuel gas system [10].

#### 1.3 Research Program

The proposed process of ligand exchange is beneficial in the prevention of these pollution problems. Also, the recovered ligand is more concentrated and could be economical for reuse. A continuous industrial-scale application of ligand exchange would involve two steps:

- Removing the ligand from aqueous solution by loading it onto the water-sorbed exchange sorbent.
- Regenerating the metal-resin sorbent with an expendable, non-contaminating ligand for further cyclic use.

This research program illustrates the potential of ligand exchange to remove amines from aqueous process streams. It has some major objectives:

- Experimental study of fixed-bed sorption. The process should be mathematically modelled from a fundamental approach to permit design of an appropriate industrial operation.
- Appraisal of the effectiveness of fixed-bed regeneration. Thus, the ligand recovery potential is measured.

The study is outlined in four phases:

- Experimentation. A description of the chemical reagents and the ligand exchanger preparation is given. The required experimental equipment is detailed along with the operating procedures. Also, appropriate analytical techniques are defined.
- Model Parameter Estimation. The batch experimental data are used to determine fundamental model parameters.
- Exchange Column Models. The ligand exchange column simulators are described and developed.

4. Evaluation of Experimental Results. Model parameter evaluations are presented along with the corresponding model simulations of experimental ligand-sorption curves.

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# Chapter II

# BACKGROUND

The direct absorption of metal-amine complexes from solution by ion exchange resins was reported by Stokes and Walton in However, ligand exchange requires the metal ion 1954 [18]. to reside in the ion exchange resin as prospective ligands are removed from solution. Helfferich first defined this term in 1961 [19]. process can be used most This advantageously when the proper metal ion is chosen. The metal ion must be capable of forming a stable complex with the ligand(s) of interest; tabulated equilibrium constants give a measure of this characteristic [20,21]. Helfferich qave а theoretical and guantitative treatment of equilibria [22]. In defining the ligand-exchange ligand-exchange capacity, he noted that several ligand molecules may complex with a single metal ion. Thus, the strength and specificity of the metal-ligand complex formation affords some distinct advantages to ligand exchange over physical adsorption or ion exchange. It is possible to achieve a higher sorbent capacity for complexing aqueous contaminants since non-complexing solutes are not Also, ligand-exchange selectivity, obtained chemisorbed. from the differences in complex strengths, suggests

applications in chromatographic separations [23] and multicomponent sorption operations.

Displacement of the complexing metal ion (by ion exchange with other cations in the external solution) interferes with ligand exchange. The resulting complex formation in the solution would counteract ligand sorption (exchange of ligands for solvent molecules in the metal ion solvation shell) or ligand exchange (displacement of other ligands previously complexed with the metal). Helfferich noted that the most obvious remedy is to choose a resin with ionogenic groups which partially complex and electrostatically attract the metal [19]. Such protection against metal ion bleed is achieved at a sacrifice in ligand-exchange capacity since the resin ionogenic groups block the metal coordinative Other studies report the affect of various ion valences. exchange resins on amine separation by ligand exchange [24-28]. Some of these reviews monitor the use of chelating resin in the exchange process. The chelating resins give strongest metal-resin bond the and provide greater protection against metal ion elution. However, the carboxylic acid resin has a higher ion exchange capacity (and a correspondingly higher ligand-exchange capacity) than the chelating resin [28]. Helfferich suggested that copper(II)-carboxylic acid resin could be an appropriate metal-resin sorbent offering sufficient protection against metal ion loss [22].

This premise was experimentally verified by Jeffrey [29] as he studied various metal ion-organic resin combinations and found that the copper(II)-carboxylic acid resin system showed the most promise. He used this sorbent to study the removal of ammonia by ligand exchange and found the process . to be successful even in dilute salt concentrations. Jeffrey and White [30] found some success at regenerating an ammonia-laden exchange column with warm water (temperatures greater than 25°C). This effect could have been predicted stability of ammonia-metal and amine-metal since the complexes decrease with increasing temperature [20]. Dawson [31] and Dobbs [32,33] developed this process for removing ammonia from water by complexing with copper(II) ions held on a hydrous, zirconium oxide ion-exchanger. They also demonstrated that the ligand exchange bed could be regenerated with low-pressure steam recovering a more concentrated ammonia solution. Groves and White [34] showed that the Thomas model could be used to predict loading column performance for the ligand exchange system studied by Jeffrey.

This same exchange sorbent should have some success at amine removal since the ammonia and amine nitrogen both function as electron donors in transition metal complexes. The metal-amine complex might be weaker than the corresponding ammonia complex since substituent groups will cause steric hindrance to the coordinate covalent bond.

Groves [35] has presented some experimental observations which verify this presumption for a few aliphatic amines. He again used the semi-empirical Thomas equation to successfully correlate ligand-sorption column performance for butylamine and monoethanolamine [36]. Discrepancies in performance prediction may be associated with the chemical reaction expression which governs the net sorption rate. The copper(II)-amine system forms labile complexes - the coordinated ligands exchange rapidly with free ligands. The chemisorbed resin-phase amine is thus considered to be in equilibrium with the solution-phase amine and the controlling rate process is mass transfer.

Therefore, it would prove useful to develop a rigorous model based on fundamental transport phenomena. The nonlinear equilibrium isotherm would require a numerical solution to the resulting coupled partial differential equations. A most recent work has performed an evaluation of ligand exchange for a batch sorber [37]. To date, no published work has addressed the applicability of ligand exchange for amine removal with respect to detailed performance prediction.

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#### Chapter III

#### **EXPERIMENTATION**

The applicability of ligand exchange for amine removal was determined from fixed-bed operations. Commercially interesting amines were sorbed from dilute aqueous solutions by complexing with copper ions held on cation exchange resin. Breakthrough and regeneration data were obtained for the fixed-bed operation. These data were compared with mathematical predictions. The mathematical models require parameters in the form of equilibrium fundamental expressions and effective diffusion coefficients. Thus, a complete experimental evaluation of this project was obtained from the analysis of batch equlibrium, batch sorption and fixed-bed column operating data.

### 3.1 Chemicals and Ligand Exchanger Preparation

The validity of the experimental results depends on the quality of the materials and chemicals used. This information, for the ion exchange resin and other important reagents, is provided in Table 1.

The ligand exchanger was prepared by loading the cationic sites of the carboxylic acid resin with divalent copper. The resin was dry-sieved for a 20/40 mesh size range. An

<u>Table 1</u> : Chem	ical Reagent Information
Reagent	Product Specification
Amberlite@ IRC-50 C.P. (Mallinckrodt Chemical Works)	Apparent density 0.67 g/ml Mesh size wet 20-50 mesh Void volume 35-40% Moisture capacity 43-53% Exchange capacity 3.5-4.0 meg/ml
Amberlite <sup>®</sup> IRC-50 (Sigma Chemical Company)	Approximate moisture content 48%
CuSO₄•5H₂O (Mallinckrodt Chemical Works)	Assay 99.54%
NaOH (Mallinckrodt Chemical Works)	Assay
p-Benzoquinone (Aldrich Chemical Company, Inc.)	Assay
Ethyl alcohol (Midwest Solvents Company of Illinois)	USP Absolute 200 proof
Diglycolamine <sup>®</sup> (DGA) (Aldrich Chemical Company, Inc.)	Assay 98% b.p 218-224°C density 1.460
Butylamine (Eastman Kodak Company)	
2-Amino-2-methyl-1- propanol (Aldrich Chemical Company, Inc.)	Assay
Triethylamine (EM SCIENCE)	b.p 88-90°C

appropriate weight of this resin was first treated with an excess of 1 M NaOH solution (the amount of sodium in solution was greater than the ion-exchange capacity). The resin was then intermittently stirred in this solution for After pouring the solution off the resin, it was one hour. treated similarly with another aliquot of the NaOH solution. The supernatant NaOH solution was decanted and the resin was washed with distilled water for 15 minutes. After two more water washes, the sodium-sorbed resin was treated with two portions of 0.2 M CuSO<sub>4</sub> solution just as it was treated with NaOH. After three water washes, the copper-loaded resin was ready for experimental use [29, p.17]. The sorbent sample weights were conveniently recorded in the resin hydrogen form since the copper loading was fairly constant at 5.8 milliequivalents per gram of exchange resin (approximately equal to the reported ion-exchange capacity of 5.2 meq/g). For this experimental measure, the copper was analyzed by iodometry.

### 3.2 Apparatus Operation

Each experimental apparatus gives fundamental properties of the metal-resin sorbent for ligand exchange. The corresponding data provided important information for the design of an industrial-scale ligand exchange operation; isotherm parameters, diffusion coefficients, exchange column performance and sorbent capacity.

# 3.2.1 Equilibrium Equipment

Ligand sorption isotherms were obtained from mathematical analysis of batch experimental data. The equilibrium apparatus is pictured in Figure 2. A 0.2 to 0.3 g sample of copper-complexed, carboxylic acid resin was charged with a 120-ml volume of ligand feed solution to a 125-ml Erlenmeyer A number of these flasks were affixed in a flask. constant-temperature shaker bath. After 24 hours at the desired temperature (±1°C), the equilibrium solution was sampled. This time duration was found to be sufficient by ammonia sorption using testing up to a three-day equilibration period. Air from the air tube displaced a solution sample through the submerged sampling port tube, a water-cooled condenser and to the sample flask. The sampling port tube is equipped with a small-mesh wire screen to inhibit the passage of resin particles with the solution sample. The equilibrium amount of ligand on the resin was determined from the difference of the charge and equilibrium In this material balance, ligand solution concentrations. hold-up in the resin interstices was negligible since the total resin-particle pore volume was no more than 0.2% of the equilibrium solution volume. Control samples (ligand solutions with no sorbent) were obtained at different concentrations to ensure minimal vaporization losses in the experimental technique.



Figure 2: Batch Equilibrium Apparatus

# 3.2.2 Batch Sorber

Agitated vessels containing slurries of adsorbent, or catalyst, have been used for many years as adsorbers for pollutant removal and as reactors [38]. Lately, these batch processes for water treatment have been replaced by The design of these industrial columns fixed-bed columns. will require suitable models for which parameters can be obtained with little experimental effort. Although the agitated vessel is not used as much commercially as in the it remains a convenient laboratory apparatus for past, parameter estimation. Batch sorption experiments can provide representative intraparticle diffusivities when the range of feasible column operating performed in conditions.

Many different designs for batch adsorption have been proposed in the literature. A recent review of adsorption vessels is given by Friedrich et al. [39]. It shows that the experimental design can influence the validity of derived model parameters. The design of a batch-contact apparatus must closely approximate the assumptions of the mathematical description to achieve model-data agreement. Most model developments assume ideal mixing with each sorbent particle sorber solution subjected to the same environment. Therefore, it was decided to freely suspend the sorbent particles in the sorption vessel fluid with sufficient agitation. Effective sorbent-phase diffusivities were

determined from the batch sorption equipment shown in Figure 3.

The 1000-ml resin kettle was filled with 900 ml of ligand The batch sorber was sealed and immersed in feed solution. a constant-temperature bath. A 6 to 10 q sample of copper-loaded resin was prepared and placed in 100 ml of water. An impeller speed of 500 rpm was sufficient to uniformly suspend the metal-resin sorbent in the sorber After setting the impeller speed, the exchange bath. sorbent was guickly slurried into the batch sorber. The solution was sampled with a 2-ml syringe at predetermined times. These samples were analyzed to obtain a traditional concentration decay curve.

The syringe needle was surrounded by a small-mesh wire screen, the sample cage, to prevent the passage of sorbent particulates with a solution sample. However, this exchange sorbent proved to be very durable as there was no observable size reduction during these experimental runs. The time required for sorbent-slurry addition was approximately 10 to 15 seconds. This time was always small with respect to the transient response since the total amount of sorbent was carefully controlled. The sample aliquots represented only 0.2% of the sorber volume. The total volume change during a sorption run was 2 to 2.6% which was small enough to be ignored in the data analysis.



Figure 3: Batch Sorber Unit
# 3.2.3 Ligand Exchange Column

Breakthrough and regeneration curves were obtained using the ligand exchange column pictured in Figure 4. A 1.5 to 2.5 g sample of copper-treated resin was charged to the 0.84-cm diameter fixed-bed section. This section is essentially a modified condenser in which the metal-resin is supported on the top and bottom by a layer of glass wool. A ligand solution was fed at a constant head and the flow was regulated at the column exit with a peristaltic pump. This solution flowed up through the exchange column bed at 1 to 3 ml per minute and ambient temperature (21 to 25°C). The effluent samples, collected in 50 to 75 ml aliquots by a fraction collector, were analyzed to determine the amine concentration. There was a slight expansion of the bed during loading because of ligand uptake. This did not significantly affect the model predictions.

The three-way valve permitted the same exchange bed sorbent to be subjected to both loading and regeneration conditions. The metal-resin, loaded with the particular ligand, was treated with hot water to regenerate the column by removing the sorbed species. The ligand exchange bed was first heated to the regeneration temperature by the water jacket (requiring 20 to 30 minutes). The water-jacketed, fixed-bed section is long enough for ambient feed water to achieve the regeneration temperature (40 to 60°C) as it reaches the sorbent bed. The jacketed portion of the



Figure 4: Ligand Exchange Column Schematic

fixed-bed section is approximately 30 cm long and the exchange sorbent bed occupies 6 to 10 cm of this length. The thermal entry length, 20 to 24 cm, was verified (for the proposed temperature range) by thermocouple measurement of the bed-inlet temperature. Thermocouple measurements were also used to correlate the bed temperature with that of the hot water bath (for the jacket feed water). The column feed flowrate was regulated at 1 to 2 ml per minute to minimize dilution of the recovered ligand. The effluent was cooled by ice water condensers to avoid vaporization losses. Samples were collected in 10 to 40 ml portions to get a well-defined elution curve. The feed water was boiled before use to drive off dissolved CO. Nonetheless, there was some bubble formation in the exchange bed voidage during regeneration operations. This occurrence undoubtly caused flow-channeling and was expected to influence performance In any case, the experimental data allowed an predictions. evaluation of the system for ligand-recovery potential.

## 3.3 Analytical Procedures

The amine concentration for batch equilibrium and exchange column liquid samples was determined by titration. The titrant was a dilute hydrochloric acid solution and methyl orange or bromocresol green was used as the indicator. Comparison of duplicate titrations using bromocresol green indicator gave a standard deviation of 0.6 ppm with an

average concentration of 13.4 ppm for diglycolamine. The batch sorber samples were too small to analyze by titration. A few spectrophotometric techniques for amine analysis were found ineffective in attempted and the required concentration range [40-42]. Finally. the procedure of [43] was successfully adapted to analyze the Hassan et al. aqueous amine solutions by spectrophotometry. A 1-ml portion of 0.01 M ethanolic p-benzoquinone was added to a 1-ml sample of 15 to 200 ppm aqueous amine. The samples were shaken, heated in a 50°C water bath for 30 minutes and diluted with pure ethanol. The percent transmittance of the resulting colored product was measured at 510 nm against an aqueous blank. The amount of diluent, 4 to 10 ml, was adjusted to give a spectrophotometric response in the range of 30 to 80% transmittance. The unknown amine concentration was determined from a calibration curve prepared using standard amine solutions. A typical spectrophotometric response curve for butylamine is shown in Figure 5.

The successful application of ligand exchange requires the complexing metal ion to remain immobilized on the resin. Therefore, the liquid samples of the batch sorber and ligand exchange column were also analyzed for the copper ion to quantify the metal loss. Atomic absorption spectrophotometry was used to measure copper concentrations in the range of 1 ppm to 20 ppm. The absorption readings were related to solution concentrations by means of a calibration curve as illustrated in Figure 6.



Figure 5: Spectrophotometric Determination of Butylamine



Figure 6: Atomic Absorption Analysis of Copper

#### Chapter IV

#### MODEL PARAMETER ESTIMATION

Modelling projections of fixed-bed column concentration history can be truly predictive only when they are based on derived from independent parameters experimental observations. To this end, the equilibrium distribution of the amine ligand between the metal-resin sorbent and the aqueous solution phase was determined from separate batch experiments. Also, batch kinetic studies were conducted to evaluate an effective diffusivity of the amine in the copper-loaded, carboxylic acid resin. The resulting model parameters were determined within the operating range of the ligand exchange column.

## 4.1 Ligand-sorption Equilibria

A quantitative theoretical treatment of ligand-sorption equilibria is not feasible due to the absence of stability constant values. The Langmuir isotherm provides a reasonable substitute because of its simple form and acceptable accuracy.

#### 4.1.1 Overview

Ligand exchange is very similar, in many respects, to ion In each process, molecular species are exchanged exchange. - usually in stoichiometrically equivalent amounts - between the solid ion exchanger and an external solution [19]. Analogous to the ion-exchange capacity, a ligand-exchange capacity of a metal-loaded resin can be defined as the number of available coordinative sites per unit weight or metal ion the resin [22]. A with an volume of electrochemical valence  $z_m$  associates with  $z_m$  ionic groups of the resin. With  $N_m$  coordination sites on this metal ion, ligand-exchange capacity X<sub>1</sub> is related to the the ion-exchange capacity X<sub>i</sub> by the relation

$$x_{1} = \frac{x_{1}N_{m}}{z_{m}}$$
(4-1)

The ligand content of a metal-resin can exceed this capacity when "free" ligands are sorbed and can fall short of the capacity when complexing is incomplete ( such as when the resin ionogenic groups occupy the coordinative valences of the metal ion). This analogy warrants the expression of ligand-exchange equilibria just as ion-exchange equilibria, in terms of exchange isotherms and separation factors.

Complex formation, however, is definitely a more specific interaction than physical adsorption or ion exchange. It

provides a very strong "driving force" for ligand sorption. Ligand exchangers sorb ligands efficiently , utilizing almost their full capacity even when the ligand concentration in the external solution is extremely low (if the complexes with the metal ion are strong). Ligand-sorption isotherms thus differ from ordinary sorption isotherms because uptake from dilute solutions is much higher and saturation of the sorbent is achieved at much lower solution concentrations [4].

The quantitative treatment of ion-exchange equilibria proves to be inadequate for ligand-exchange equilibria. Factors that are unique to this process must be taken into account:

- Blocking of metal coordinative valences by ionogenic groups of the resin.
- 2. Formation of coordinatively unsaturated complexes.
- 3. Formation of "mixed" complexes where different ligand species vie for the coordinative sites (in multicomponent ligand-exchange equilibria).
- Sorption of "free" ligands in addition to the complexed ones.

This theory was fully developed by Helfferich [22]. He further assumed that the ligands do not displace resin groups from the metal-ion coordinative sites they occupy. The resulting mathematical formulation for ligand sorption (with some approximations) can be stated as

$$\frac{M_{1}}{m_{1}} = 1 + \frac{M_{m} \sum_{i=1}^{p} i K_{i}m_{1}}{P} (i-1)$$

$$(4-2)$$

$$\sum_{i=0}^{p} K_{i}m_{1}^{i}$$

where  $M_1$  and  $m_1$  represent the molalities of the ligand in the resin and external solution phase, respectively. M<sub>m</sub> is the resin-phase molality of the metal which has a maximum ligand number P. The K<sub>i</sub> are the molal cumulative Bjerrum stability constants of the complexes with ligand numbers i These model equations were shown to agree very  $(K_0 \text{ is } 1).$ well with experimental data [22]. this manner, In ligand-exchange equilibria can be predicted from the respective complex-stability constants which are usually available in the literature [20,21]. Groves et al. [34] used this method to describe the equilibrium relationship for ammonia on copper-loaded, carboxylic acid ion exchanger. Nonetheless, the required stability constants for the amines in this study were not found in the literature. Independent experimental observation is necessary to define the exchange equilibria. Rather than attempt a rigorous evaluation of appropriate complex-stability constants, the а more empirical model of the ligand-exchange equilibria was expedient.

The uptake of amines by the metal-resin increases with increasing concentration of the external solution [35]. The

sorption isotherm usually has a convex curvature. There are many isotherm equations which can simulate this effect. Fritz and Schlunder [44] correlated the adsorption equilibria of organic solutes in water with a general empirical equation of the following form:

$$q_{i} = \frac{a_{i}C_{i}^{b_{i}}}{d_{i} + \sum_{j=1}^{n} a_{j}C_{j}^{b_{j}}}$$
(4-3)

The parameters  $a_i$ ,  $b_i$ , and  $d_i$  are fitted to the data for solute i of n components. Liapis and Rippin [45] have shown that the Freundlich equation

$$q = aC^{b}$$
 (4-4)

and the Langmuir equation

$$\mathbf{q} = \frac{\mathbf{aC}}{\mathbf{1} + \mathbf{bC}} \tag{4-5}$$

can be obtained as special cases of equation (4-2). Both the Langmuir and the Freundlich isotherm are popular in the characterization of dilute-solution adsorption for solid-liquid systems. However, the Langmuir isotherm has been previously used to model ligand-sorption equilibria [35,36]. Based on this evidence and the potential for extension to multicomponent equilibria [45], the Langmuir isotherm was chosen to model the amine-sorption equilibria of this work.

# <u>4.1.2</u> Langmuir Constants

The Langmuir constants were obtained from a nonlinear least squares fit of the data. A constrained pattern search technique was used to perform the two-dimensional parameter optimization [46]. Initial guess values for the search were obtained from estimations of the slope at the origin and the asymptote. An equilibrium curve and Langmuir model for butylamine is pictured in Figure 7. This equilibrium relationship is often non-dimensionalized with respect to reference values  $q_o$  and  $C_o$  to get

$$Q = \frac{\alpha U}{1 + (\alpha - 1)U} \qquad (4-6)$$

The value  $q_0$  represents the sorbed phase concentration in equilibrium with  $C_0$  and  $q = C_0 b + 1$ . With this Langmuir form, a family of curves can be developed as shown in Figure 8.

A statistical evaluation of the optimum Langmuir parameters can be obtained by using the "Method of Maximum Likelihood" [47,48]. An approximate (1-H)x100% joint confidence region for a and b can be defined by the equation



Figure 7: Butylamine Equilibrium at 22°C



Figure 8: Dimensionless Langmuir-type Equilibrium

$$B = S \left[1 + \frac{p}{(n-p)} F_{H}(p, n-p)\right]$$
(4-7)

In this formula, the contour B encloses the proposed region and is a function of sum-of-squared-errors minimum S and the F-distribution. Also, p is the number of parameters (two in this case) and n is the number of experimental observations. The contour boundary was outlined by 1) choosing a value of the parameter b and 2) performing a Newton-Rhapson search with synthetic division to find the values of the parameter minimize the difference between B and a that the sum-of-squared-errors. By implementing the above procedure through an incremental range in b, the confidence contour is defined by the corresponding roots a. In this manner, the 95% joint confidence region was outlined for the previous butylamine isotherm parameters. This contour is shown in Figure 9.



Figure 9: The 95% Joint Confidence Region for Butylamine Langmuir Parameters at 22°C

# 4.2 Diffusion Coefficients

Mass transfer is known to be the rate-controlling step in most physical adsorption and ion exchange processes. This should be the case for ligand exchange since there are kinetic limitations. effectively no Α reasonable, diffusion quantitative estimate of an intraparticle coefficient can be obtained from batch sorption experiments. However, these mathematical models must reflect a knowledge of the sorbent internal structure along with other mass transfer resistances inherent to the experimental design. A general discussion is given in which these important points are related to ligand-exchange diffusivities. Appropriate batch sorber models are developed for both linearized isotherms and a Langmuir representation of ligand-sorption equilibria.

### 4.2.1 General Aspects

Effective diffusion coefficients can be determined for many types of "porous media." This term is loosely applied to all types of systems consisting of a coherent, but not necessarily rigid, structural framework with interstices ("pores") that permit diffusion and other mass transfer processes to occur in the medium [4]. For this definition of porous media, two extremes can be defined:

 "Macroreticular" solids with a netlike, rigid structure and macroscopic pores;

 "Microreticular" gels with molecular, flexible hydrocarbon chains as the framework.

The structure of many porous solids fits somewhere between these extremes. These non-uniformities in the porous matrix complicate the description of intraparticle diffusion. Some macroreticular adsorbents can be roughly considered as biporous structures. Microscopic descriptions of the diffusional process generally depict two regions of different transport rates, macropores and micropores Amberlite<sup>®</sup> IRC-50 resin has a macroreticular **[49-51]**. structure [52]. An electron micrograph shows the framework to be composed of aggregates of gel microspheres. However, the pore-size distribution is unimodal at 800 Å with a pore-size radius range of 200 to 2000 Å (characteristics for the dry structure). The resin properities were assumed to be unaffected by the inclusion of copper in the matrix. This information served as a useful first-approximation in describing the intraparticle mass transfer.

Solute transport in porous media is usually modelled according to the classic Fickian laws for diffusion. Do and Rice [53] give a complete development of this transport mechanism. For a spherical porous sorbent, the radial transport flux of a sorbate per unit area normal to the flux is given by

$$J = - \left[ \epsilon_{p} D_{p} \frac{\partial C_{p}}{\partial r} + \rho_{p} D_{s} \frac{\partial q}{\partial r} \right]$$
(4-8)

The first term represents the pore-phase flux and the second term gives the surface (sorbed-phase) flux contribution. There are two limiting cases that can be derived from this relation: 1) pore diffusion and 2) surface or solid diffusion.

When pore diffusion is the only mass-transfer mechanism inside a sorbent particle, this flux is limited by three main factors:

- The pore cross-sectional area is the only true area available for diffusion.
- The diffusion pathway for a solute molecule in each pore is tortous.
- 3. The sorbate molecular diameter and the sorbent pore diameter may be of comparable magnitude.

Satterfield et al. [54] and Chantong et al. [55] have addressed these effects in detail. They give the effective diffusivity as

$$D_{e} = \frac{D\varepsilon_{p}}{\lambda} \cdot F_{r} \qquad (4-9)$$

The restrictive factor F, involves steric hindrance (partitioning of the solute across the pore-outside boundary due to geometric exclusion) and hydrodynamic friction (induced drag on solute molecules as a result of pore-wall and/or sorbed-phase proximity). The value of the effective diffusivity increases to that of the molecular diffusion coefficient in the absence of the aforementioned restrictions. However, this mathematical description becomes inadequate when surface diffusion is important.

Surface diffusion has been given much attention in recent literature. Using a two-resistance batch adsorption model (film transfer and intraparticle diffusion), Furusawa and Smith [38] found the pore-volume diffusivity for aqueous benzene in activated carbon. This value was about ten times the corresponding molecular diffusion greater than coefficient. They accounted for this discrepancy by proposing that surface migration on the pore walls was After including surface diffusion in the important. transport mechanism, it was found to be the dominant contribution to the observed total-effective diffusivity. Komiyama and Smith [56,57] also found that surface diffusion can dominate intraparticle mass transport in liquid-filled These authors studied the batch adsorption of pores. aqueous benzaldehyde onto Amberlite® adsorbents. Surface diffusion was 5 to 14 times the contribution of pore-volume transport at high adsorption capacities and low external

solution concentrations. Also, Moon and Lee [58] deduced that surface diffusion was important in phenol batch adsorption onto activated carbon at low aqueous concentrations. This element of intraparticle diffusion may be unimportant for ligand exchange. If the metal-ligand complex is strong, the ligand should be immobilized in its chemisorbed state.

There are many experimental methods in the literature for diffusivity estimation. Weber et al. [59-61] have recently shown the short-bed adsorber method to accurately predict mass-transfer parameters for fixed-bed adsorbers. Helfferich also outlines the shallow-bed technique for diffusivity estimation [4, p.311]. Nevertheless, batch sorbers still give an accurate and more convenient estimation of mass transfer parameters.

#### 4.2.2 Batch Sorber Models

Each batch sorber model considers an isothermal, well-mixed volume of solution V suddenly subjected to a volume  $V_p$  of ligand-exchange sorbent. With good mixing, the sorbent remains uniformly dispersed throughput the fluid phase. The composition of the bulk fluid C<sub>o</sub> is related to the volume-average sorbent concentration according to the material balance

$$v \frac{dc_{b}}{dt} = - v_{p} \rho_{p} \frac{dq_{a}}{dt}$$
 (4-10)

Initial conditions are

$$c_{b} = c_{0} \tag{4-11}$$

$$q_a = 0 \tag{4-12}$$

The dimensionless form according to  $\mathbf{C}_{\mathbf{e}}$  and  $\mathbf{q}_{\mathbf{e}}$  gives

$$\frac{dv_{b}}{dt} = -\frac{1}{\xi} \frac{dQ_{a}}{dt} \qquad (4-13)$$

$$\xi = \frac{VC_0}{V_p \rho_p q_0} = \frac{VC_0}{M_r q_0} ; \quad M_r = \rho_p V_p$$

This equation integrates to

$$u_{b} = 1 - Q_{a}/\xi$$
 (4-14)

The sorbent-phase material balance, assuming a spherically symmetric pore structure, can be described by the differential equation

$$\varepsilon_{\mathbf{p}} \frac{\partial C_{\mathbf{p}}}{\partial t} + \rho_{\mathbf{p}} \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( \varepsilon_{\mathbf{p}} D_{\mathbf{p}} \frac{\partial C_{\mathbf{p}}}{\partial r} + \rho_{\mathbf{p}} D_{\mathbf{s}} \frac{\partial q}{\partial r} \right) \right] (4-15)$$

The boundary and initial conditions are

$$c_p = q = 0; 0 \le r < R t = 0$$
 (4-16)

$$\frac{\partial C_p}{\partial r} = \frac{\partial q}{\partial r} = 0 ; r = 0, t \ge 0 \qquad (4-17)$$

$$\frac{\mathbf{V}_{\mathbf{p}}\rho_{\mathbf{p}}}{A_{\mathbf{p}}}\frac{d\mathbf{q}_{\mathbf{a}}}{d\mathbf{t}} = \mathbf{k}_{\mathbf{f}}(\mathbf{C}_{\mathbf{b}} - \mathbf{C}^{\star}) = \left[ \epsilon_{\mathbf{p}}\mathbf{D}_{\mathbf{p}}\frac{\partial\mathbf{C}_{\mathbf{p}}}{\partial\mathbf{r}} + \rho_{\mathbf{p}}\mathbf{D}_{\mathbf{s}}\frac{\partial\mathbf{q}}{\partial\mathbf{r}} \right] ;$$
  
$$\mathbf{r} = \mathbf{R}, \mathbf{t} > 0 \qquad (4-18)$$

$$q = f(C_p) ; 0 \le r \le R, t \ge 0$$
 (4-19)

Equation (4-18) represents film transfer at the particle-solution interface and equation (4-19) denotes equilibrium between the pore and complexed phases throughout the sorbent matrix. These equations may be simplified with certain assumptions.

#### 4.2.2.1 Linearized Isotherm

The equilibrium expression in equation (4-5) can be linearized over the operating concentration range. Then, the transient-diffusion equation (4-15), for constant diffusivities, reduces to

$$\frac{\partial Y}{\partial \tau_1} = \frac{1}{\zeta^2} \frac{\partial}{\partial \zeta} \zeta^2 \frac{\partial Y}{\partial \zeta}$$
(4-20)

with the boundary condition

$$\frac{\partial Y}{\partial \zeta} = sh_1(U_b - Y); \quad \zeta = 1, \ \tau_1 > 0$$
 (4-21)

These equations can be related to pore, solid and combined (pore and surface) diffusion by defining the dimensionless quantities as shown in Table 2. Do and Rice summarize these dimensionless quantities for pore and solid diffusion [62].



The solution to the above equations is

$$U_{b} = \frac{\xi_{1}}{\xi_{1} + 1} + \frac{6}{\xi_{1}} \sum_{n=1}^{\infty} P(w_{n}) \exp(-w_{n} \tau_{1}^{2}) \qquad (4-22)$$

where

$$[P(w_n)]^{-1} = (3/\xi_1 - w_n^2/Sh_1)^2 + 3(3/\xi_1 - w_n^2/Sh_1) + w_n^2(1 + 2/Sh_1)$$

and  $w_n$  are the roots of the transcendental equation

$$[-3/\xi_{1} + (1/sh_{1} - 1)w_{n}^{2}]sin w_{n} + (3/\xi_{1} - w_{n}^{2}/sh_{1})w_{n} cos w_{n} = 0$$
(4-23)

Edeskuty et al. gives this analytical solution for the pore-diffusion case [63]. The solid-diffusion case can be obtained from the heat-transfer solution given by Munro et al. [64]. Later, Costa et al. [65] showed that the solution for the combined-diffusion problem takes the same form. The form of this solution is simpler when the sorbent concentration is assumed to obey a time-dependent parabolic response

$$Y = a_0(t) + a_2(t) \zeta^2$$
 (4-24)

Rice [67] derived the corresponding solution as

$$U_{\rm b} = \frac{\xi_1}{\xi_1 + 1} + \frac{1}{\xi_1 + 1} \exp\left[\frac{-15(\xi_1 + 1)\tau_1}{\xi_1(1 + 5/{\rm Sh}_1)}\right] \qquad (4-25)$$

This substitution of the parabolic profile for the diffusion equation (4-20) has been validated for dimensionless times greater than 0.05 For nominal values of  $\mathcal{E}_1$  and  $\mathrm{Sh}_1$ , the error is within 10% at smaller dimensionless times [62]. Equation (4-22) has been used for nonlinear adsorption isotherms, getting a mean slope of the equilibrium curve (K) in the experimental concentration range [38,66]. However, linearization of the sorption isotherm can result in significant error in the determination of diffusivities [68]. Therefore, the sorption process was modelled with the Langmuir isotherm and solved numerically.

## 4.2.2.2 Pore Diffusion

Pore diffusion will be the only intraparticle transport mechanism when the ligand complexation is strong enough to immobilize the chemisorbed solute. The appropriate sorbent-phase material balance is obtained by assuming that  $D_s$  approaches zero

$$\varepsilon_{\mathbf{p}} \frac{\partial C_{\mathbf{p}}}{\partial t} + \rho_{\mathbf{p}} \frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 (\varepsilon_{\mathbf{p}} D_{\mathbf{p}} \frac{\partial C_{\mathbf{p}}}{\partial r}) \qquad (4-26)$$

For a constant  $\epsilon_{\rm P} D_{\rm P}$  , this equation can be non-dimensionlized as

$$[1 + \frac{g'(U_p)}{\gamma}] \quad \frac{\partial U_p}{\partial \tau_p} = 4z \frac{\partial^2 U_p}{\partial z^2} + 6 \frac{\partial U_p}{\partial z}$$
(4-27)  

$$g(U) = Q = \alpha U / [1 + (\alpha - 1)U]$$

$$g'(U) = \alpha / [1 + (\alpha - 1)U]^2$$

with the boundary condition reducing to

$$sh_p(U_b - U_p) = 2\sqrt{z} \frac{\partial U_p}{\partial z}$$
;  $z = 1$ ,  $\tau_p > 0$  (4-28)

$$sh_p = \frac{k_f R}{\epsilon_p D_p}$$

The average particle composition is related to the flux at the particle surface by

$$\frac{1}{3\gamma} \frac{dQ_a}{d\tau_p} = 2\sqrt{z} \frac{\partial U_p}{\partial z} ; z = 1, \tau_p > 0 \qquad (4-29)$$

The symmetry condition is satisfied identically by the spatial coordinate transformation  $z = \zeta^2$ . The model equations were solved by orthogonal collocation [69,70].

Equation (4-27) was discretized at N interior collocation points

$$[1 + g'(U_{pi})/\gamma]^{-1} \begin{bmatrix} N+1 \\ \Sigma \\ j=1 \end{bmatrix} T_{ij} U_{pj} = \frac{dU_{pi}}{dT_{p}}$$
$$1 \le i \le N \qquad (4-30)$$

Another differential equation arises from the discretization of equation (4-29)

$$\frac{dQ_a}{d\tau_p} = 6\gamma \sum_{j=1}^{N+1} A_{N+1,j} U_{pj} \qquad (4-31)$$

The boundary condition of equation (4-28) reduces to

$$2\sum_{j=1}^{N+1} A_{N+1,j} U_{pj} = Sh_p(U_b - U_{pN+1})$$
(4-32)

The pore concentration at the surface of the particle is obtained from this equation. Substituting this value into equations (4-30) and (4-31), they become

$$Dep_{i} \left[ \sum_{j=1}^{N} (T_{ij} - \frac{2 T_{i,N+1} \cdot A_{N+1,j}}{2 A_{N+1,N+1} + Sh_{p}}) U_{pj} + \frac{T_{i,N+1} \cdot Sh_{p} \cdot U_{b}}{2 A_{N+1,N+1} + Sh_{p}} \right]$$
$$= \frac{dU_{pi}}{d\tau_{p}} ; 1 \le i \le N \qquad (4-33)$$
$$Dep_{i} = [1 + g'(U_{pi})/\gamma]^{-1}$$

$$\frac{dQ_a}{d\tau_p} = \frac{6\gamma Sh_p}{(2A_{N+1,N+1} + Sh_p)} \begin{bmatrix} N \\ \Sigma \\ j=1 \end{bmatrix} A_{N+1,j} U_{pj} + A_{N+1,N+1} U_{b}$$

$$(4-34)$$

The resulting set of N+1 differential equations were integrated with the Livermore Solver routine developed by Hindmarsh [71]. The spatial coordinate was discretized at the zeroes of the orthogonal polynomials  $P_N^{(1, 1/2)}(z)$ . These polynomials were suggested by Villadsen and Stewart [69] as they modelled similar boundary-value problems. Rice et al. [62,67] reported on the validity of analogous approximating polynomials. Eighth-order (N=8) polynomials were found to be sufficient for differences in the fourth digit as compared to higher order approximations (for nominal parameter values). This solution technique was coupled with a constrained pattern search [46] to determine the best-fit diffusivity for an experimental run. For a given diffusion coefficient, the model and experimental dimensionless times were matched (to within the integration interval) to obtain the error in U . The objective of the optimization was to minimize the sum of these squared errors. Costa et al. [51] used a similar minimization procedure called the "concentration criterion." The numerical method was compared with the linear-isotherm, analytical solutions of Amundson et al. [63,64]. The agreement was found to be

excellent with differences in the third and fourth digit only at small dimensionless times.

authors have solved these model Other equations [58,72,73]. Liapis and Rippin [45] solved the binary-adsorption case by orthogonal collocation. Using the same solution technique, Neretnieks [74] solved the above equations calculating an array of integration weights to determine the average-sorbent concentration. In the above derivation, equation (4-34) is used instead adding one more equation to the set of ordinary differential equations (ODEs). This additional equation is easily handled by the sophisticated solver package. A typical batch sorber response was calculated in 15 to 20 seconds by an IBM 4341 FORTRAN program.

#### 4.2.2.3 Solid Diffusion

The solid diffusion model is commonly used in adsorption processes [58,72,75]. In this model, the pore-phase holdup is neglected since the sorption capacity is high. Equation (4-15) simplifies to

$$\rho_{\mathbf{p}} \frac{\partial \mathbf{q}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \left[ \varepsilon_{\mathbf{p}} D_{\mathbf{p}} \frac{\partial C_{\mathbf{p}}}{\partial \mathbf{q}} + \rho_{\mathbf{p}} D_{\mathbf{g}} \right] \frac{\partial \mathbf{q}}{\partial r} \qquad (4-35)$$

Taking an average value

51 .

$$D_{h} = \left[ \frac{\varepsilon_{p} D_{p}}{\rho_{p}} \frac{\partial C_{p}}{\partial q} \right|_{Avg} + D_{g} \right]$$
(4-36)

we get

$$\frac{\partial q}{\partial t} = \frac{D_h}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial q}{\partial r} \qquad (4-37)$$

The pseudo-homogeneous solid is in equilibrium with the external solution at the particle surface

$$q = \frac{aC^*}{1 + bC^*}$$
;  $r = R$  (4-38)

The film transfer at the particle surface is defined as

$$\rho_{\mathbf{p}} \mathbf{D}_{\mathbf{h}} \frac{\partial \mathbf{q}}{\partial \mathbf{r}} = \mathbf{k}_{\mathbf{f}} (\mathbf{C}_{\mathbf{h}} - \mathbf{C}^{*}); \mathbf{r} = \mathbf{R}, \mathbf{t} > 0 \qquad (4-39)$$

and the average sorbent concentration is

$$V_p \frac{dq_a}{dt} = A_p D_h \frac{\partial q}{\partial r}; r = R, t > 0$$
 (4-40)

After the dimensionless forms are derived, the collocation forms of equations (4-37), (4-39) and (4-40) are obtained as before

$$\sum_{j=1}^{N+1} T_{ij} Q_j = \frac{dQ_i}{d\tau_h} ; 1 \le i \le N$$
 (4-41)

$$\sum_{j=1}^{N+1} A_{N+1,j} Q_j = Sh_h(U_b - U^*)$$
 (4-42)

$$\mathrm{Sh}_{\mathrm{h}} = \frac{\mathrm{k}_{\mathrm{f}} \mathrm{C}_{\mathrm{0}} \mathrm{R}}{\mathrm{\rho}_{\mathrm{p}} \mathrm{D}_{\mathrm{h}} \mathrm{q}_{\mathrm{0}}} = \frac{\mathrm{k}_{\mathrm{f}} \mathrm{\gamma} \mathrm{R}}{\mathrm{\epsilon}_{\mathrm{p}} \mathrm{D}_{\mathrm{h}}}$$

$$\frac{dQ_{a}}{dt_{h}} = 6 \sum_{j=1}^{N+1} A_{N+1,j} Q_{j}$$
 (4-43)

Equation (4-38) is converted into an "ultra-stiff" ODE at the particle surface

$$\psi \frac{dQ_{N+1}}{d\tau_{h}} = \alpha U^{*} - [1 + (\alpha - 1)U^{*}] Q_{N+1} \qquad (4-44)$$

with  $\psi$  being used as an adjustable "stiffness factor" (a very small number). After substituting equation (4-38) for U\* in this equation, the resulting N+2 ODEs were integrated using the stiff-equations option of the Livermore solver. A stiffness factor of 10\*7 and 8 interior collocation points stabilized the solution in the fourth digit. Computation times ranged from 20 to 30 seconds for a single profile.

A nonlinear isotherm presents difficulty in model predictions for this type of parameter estimation. The Crank-Nicholson method [76] and McKay's semi-analytical solution [77] have inherent stability problems. The method of orthogonal collocation was chosen because no stability or convergence problems have been encountered in similar applications. Liapis and Rippin [45] indicate some difficulty in handling the nonlinear boundary condition for the binary-component analogous model. They join а Newton-Rhapson iterative scheme with an appropriate integration method to solve their differential-algebraic In the present development, the nonlinear boundary system. condition is transformed into a stiff differential equation as suggested by Villadsen and Michelsen [70, p. 341]. Numerical simulations were performed using both the aforementioned simplification and the explicit Langmuir boundary condition. These two solutions were compared using appropriate solver packages [71]. It was found that the stiff-differential-equation approach gave virtually the same degree of accuracy requiring approximately one-half the computing time of the differential-algebraic solution. This comparison was performed over a nominal range of model parameters.

## 4.2.2.4 Combined Diffusion

The transient diffusion equation (4-15) can be condensed to the combined-diffusion model by assuming constant diffusivities and neglecting the solute pore-phase accumulation. The pore-to-surface capacity ratios ( $\boldsymbol{x}$ ) for the present work are of the order 10<sup>\*3</sup>. Thus, neglecting the pore-phase holdup is a reasonable approximation. The diffusion-equation dimensionless form is

$$g'(U_{p}) \frac{\partial U_{p}}{\partial \tau_{c}} = \frac{1}{\zeta^{2}} \frac{\partial}{\partial \zeta} \left[ \zeta^{2} \frac{\partial}{\partial \zeta} \left[ F(U_{p}) \right] \right]$$
(4-45)  
$$F(U_{p}) = U_{p} + \Phi g(U_{p})$$

The boundary condition simplifies to

$$\operatorname{Sh}_{\mathbf{p}}(\mathbf{U}_{\mathbf{b}} - \mathbf{U}_{\mathbf{p}}) = \frac{\partial}{\partial \zeta} [F(\mathbf{U}_{\mathbf{p}})]; \zeta = 1, \tau_{\mathbf{c}} > 0 \qquad (4-46)$$

and the average ligand concentration in the metal-resin is

$$\frac{dQ_{a}}{d\tau_{c}} = 3 \, \text{sh}_{p}(U_{b} - U_{p}); \, \zeta = 1, \, \tau_{c} > 0 \qquad (4-47)$$

The collocation equations are developed as previously described

$$\frac{1}{g'(U_{pi})} \left[ \sum_{j=1}^{N} (T_{ij} - \frac{T_{i,N+1} \cdot A_{N+1,j}}{A_{N+1,N+1}}) F_{j} + \frac{T_{i,N+1} \cdot Sh_{p}(U_{b} - U_{pN+1})}{2 \cdot A_{N+1,N+1}} \right] = \frac{dU_{pi}}{d\tau_{c}} ; 1 \le i \le N+1 \quad (4-48)$$

and

$$\frac{dQ_a}{d\tau_c} = 3 \operatorname{sh}_p(U_b - U_{pN+1})$$
 (4-49)

The boundary condition in equation (4-46) has been included in the collocation equations. The extra collocation equation at the particle surface is added to avoid a stiff equation from the nonlinear boundary condition. The N+2 ODEs were integrated with the Livermore solver to simulate the batch sorber response. Neretnieks [74] and Brecher et al. [78] present solutions to this model for Freundlich and BET isotherms, respectively.

## 4.2.2.5 Model Similarities

All of the models include film transfer for the batch process. There are correlations available for transfer coefficients in this type of operation [79,80]. Furusawa and Smith [38] use the initial-slope method to determine the film transfer coefficient from concentration versus time curves. Since the batch sorber response is initially governed by film diffusion

$$v \frac{dc_{b}}{dt} = -k_{f} A_{p} C_{b} \qquad (4-50)$$

where the sorbent-solution interfacial concentration is zero early in a run. The resulting solution is

$$\ln U_{\rm b} = \frac{-3 k_{\rm f} M_{\rm r}}{R \rho_{\rm p} V} t \qquad (4-51)$$

The linear response is forced through the coordinate (0,1) and the film transfer coefficient is determined from the slope [81].

An estimation of the pore diffusivity can be obtained from equation (4-9). Experimental procedures are available to estimate molecular diffusion coefficients [82]. However, if an 11% error is acceptable, the Othmer and Thakar correlation can give a representative molecular diffusivity The restrictive effects can be ignored for this [83]. macroreticular resin. Tortuosities of 2 to 4 are commonly reported in the literature [56,57]. With this information, the expected value of the pore diffusivity can determined. If this expected value is lower than pore-diffusion-model diffusivity, surface diffusion may be significant. Thus, the solid-diffusion or combined-diffusion model may be
appropriate. The combined-diffusion model can be used to find the surface diffusivity by explicitly accounting for the pore-transport contribution as previously described. The FORTRAN programs for the nonlinear batch sorber models are given in Appendix A.

## Chapter V

#### EXCHANGE COLUMN MODELS

The response of a fixed-bed, ligand exchange column was predicted using independently-obtained model parameters. The theory for fixed-bed sorption is extensively discussed in the literature [4,84]. The following presentation gives only a few of the possible model applications. These models can account for loading and regeneration column performance. Some of the FORTRAN programs are found in Appendix B.

## 5.1 Liquid-Phase\_Material Balance

The liquid-phase material balance describes a fixed-bed of spherical exchanger particles at a uniform temperature. The inherent assumptions are:

- 1. The bed is radially and angularly symmetric.
- Axial dispersion is neglected. This assumption has been validated even for short-bed adsorbers [59,60].
- 3. The particle diameter is small in comparison with the overall bed length and the bed is macroscopically uniform.

The resulting mathematical expression is

$$\varepsilon_{\rm b} \frac{\partial C_{\rm f}}{\partial t} + \varepsilon_{\rm b} v \frac{\partial C_{\rm f}}{\partial x} + \rho_{\rm b} \frac{\partial q_{\rm a}}{\partial t} = 0 \qquad (5-1)$$

Since the exchange process is under non-dispersive conditions, the time scale can be transformed to give

$$\varepsilon_{b} v \frac{\partial C_{f}}{\partial x} + \rho_{b} \frac{\partial q_{a}}{\partial t'} = 0$$
 (5-2)

where t' = t - x/v

.

The initial and boundary conditions for ligand sorption are

$$C_{f} = C_{0} ; x = 0, t' > 0$$
 (5-3)

$$q_a = 0 ; 0 \le x \le L, t' = 0$$
 (5-4)

$$C_{f} = 0$$
;  $0 < x \le L$ ,  $t' = 0$  (5-5)

For column regeneration, the conditions are

 $C_f = 0$ ; x = 0, t' > 0 (5-6)

$$q_a = q'_0 ; 0 \le x \le L, t' = 0$$
 (5-7)

$$C_{f} = C_{0}'; \ 0 < x \leq L, \ t' = 0$$
 (5-8)

The second term in equation (5-2) is the volume-average accumulation in the exchanger sorbent. It couples the

liquid-phase material balance to that of the sorbent phase. The mathematical description of this term gives rise to the different models for a fixed-bed response.

# 5.2 Sorbent-Phase Material Balance

The ligand exchange process can be modelled with a "pseudo-kinetic" driving force and a Fickian driving force.

## 5.2.1 Ligand exchange with a Kinetic Driving Force

Thomas provided analytical solutions for the performance of fixed-bed, ion-exchange columns in which the rate of exchange is determined by second-order kinetics [85,86]. These models allow for the curved shape of the equilibrium isotherm with mass-action kinetics

$$\frac{\partial q_a}{\partial t'} = \kappa a_I \left[ c_f(q_0 - q_a) - \frac{1}{\alpha} q_a(c_0 - c_f) \right]$$
(5-9)

and Langmuir kinetics

$$\frac{\partial q_a}{\partial t'} = \kappa a_I \left| C_f(q_m - q_a) - \frac{C_0}{K_L} q_a \right|$$
 (5-10)

The resulting equilibrium expression for equation (5-9) has been given in equation (4-6). The isotherm corresponding to Langmuir kinetics is

$$\frac{\mathbf{q}_{a}}{\mathbf{q}_{m}} = \frac{\mathbf{K}_{L}\mathbf{U}}{\mathbf{1} + \mathbf{K}_{L}\mathbf{U}}$$
(5-11)

The kinetic parameter is determined from a constant-pattern assumption as outlined by Sherwood et al. [87]. The analytical solution of both equations takes a general form [88,89]. For column loading, the solution is

 $\frac{J(R_{t}N_{t},N_{t}T)}{J(R_{t}N_{t},N_{t}T) + [1 - J(N_{t},R_{t}N_{t}T)] \exp[(R_{t} - 1)N_{t}(T - 1)]}$ 

$$(5-12)$$

where

$$J(e,f) = 1 - \int_{0}^{e} \exp(-f-s) I_{0}(2\sqrt{fs}) ds$$

The solution for regeneration conditions is

v<sub>f</sub> =

 $\frac{1 - J(R_t N_t, N_t T)}{[1 - J(R_t N_t, N_t T)] + J(N_t, R_t N_t T) \exp[(R_t - 1)N_t(T - 1)]}$ 

(5-13)

The dimensionless parameters are defined in Table 3 for both kinetic equations.

Table 3: Thomas Model ParametersEquation $N_{t}$  $R_{t}$  $N_{t}T$ (5-9) $\frac{\rho_{b}\kappa a_{I}q_{0}x}{\varepsilon_{b}v}$  $\frac{1}{\alpha}$  $\kappa a_{I}C_{0}t'$ (5-10) $\frac{\rho_{b}\kappa a_{I}q_{m}x}{\varepsilon_{b}v}$  $\frac{1}{\kappa_{L}+1}$  $\kappa a_{I}(1 + 1/\kappa_{L})C_{0}t'$ 

The values of the J-function have been tabulated and are available on nomographs [87]. Hiester and Vermeulen [88] give approximations to this J-function that are applicable under certain conditions [34,36]. They also note that this function must be accurately known when evaluating equations (5-12) or (5-13), especially if the function is close to zero or unity. Tan [90-92] developed an infinite-series logarithmic expansion for the J-function

$$J(e,f) = \sum_{k=0}^{\infty} B_k(f) \exp[k\ln(e) - e - \sum_{m=1}^{k} \ln(m)]$$
(5-14)

where

$$B_{k}(f) = B_{k-1}(f) - \exp[(k-1)\ln(f) - f - \sum_{m=1}^{K-1} \ln(m)]$$
  
$$B_{0}(f) = 1$$

Liaw et al. [93] report a series truncation for a similar function that gives minimial error. With this information, the logarithmic expansion of the J-funciton was truncated to the first I terms where

$$I = 20 + Max(2e, 2f)$$
 (5-15)

This method of evaluating the J-function reproduces tabulated values [87] to the fourth and fifth digit. Tan [92] also gave a form of equation (5-12) that allows accurate results (using the properties of the J-function) and avoids numerical overflow problems:

$$\frac{1}{U_f} = 1 + \exp(G)$$
 (5-16)

where, for column loading conditions,

$$G = \ln[\sigma_1(N_t, R_t N_t T)] - \ln[J(R_t N_t, N_t T)] + (R_t - 1)N_t(T - 1)$$
(5-17)

anđ

$$\sigma_1(e,f) = 1 - J(e,f) = J(f,e)[1 - \sigma_0(f,e)/J(f,e)]$$
 (5-18)

$$\sigma_0(e,f) = -\frac{\partial}{\partial e} [J(e,f)] = \exp(-e-f) I_0 (2\sqrt{ef})$$
 (5-19)

The column regeneration response can also be calculated from equation (5-16) when

$$G = \ln[J(N_{t}, R_{t}N_{t}T)] - \ln[\sigma_{1}(R_{t}N_{t}, N_{t}T)] + (R_{t} - 1)N_{t}(T - 1)$$
(5-20)

When the Thomas model approximations [88] are appropriate, they are used instead of the above rigorous evaluations for small-parameter arguments.

Tan [92] and Sherwood et al. [87] outlined a method for designing a fixed-bed column under loading conditions. For a given set of conditions, the design problem requires the appropriate variable that will zero the equation

$$E(R_{t}, N_{t}, T, U_{f}) = \ln[\sigma_{1}(N_{t}, R_{t}N_{t}T)] + (R_{t} - 1)N_{t}(T - 1)$$
  
-`ln[J(R\_{+}N\_{+}, N\_{t}T)] - ln[1/U\_{f} - 1]

The unknown variable is determined from a Newton-Rhapson convergence scheme given

$$\frac{\partial E}{\partial x} = (R_t - 1) \left[ \frac{\partial (N_t T)}{\partial x} - \frac{N_t}{x} \right]$$

$$-\frac{1}{\sigma_1(N_t,R_tN_tT)} \left[ R_t \frac{\partial(N_tT)}{\partial x} \sigma_2(N_t,R_tN_tT) - \frac{N_t}{x} \sigma_0(N_t,R_tN_tT) \right]$$

$$-\frac{1}{J(R_{t}N_{t},N_{t}T)}\left[\frac{\partial(N_{t}T)}{\partial x}\alpha_{2}(R_{t}N_{t},N_{t}T) - \frac{R_{t}N_{t}}{x}\alpha_{0}(R_{t}N_{t},N_{t}T)\right] (5-22)$$

and

$$\frac{\partial E}{\partial t} = (R_t - 1) \frac{\partial (N_t T)}{\partial t}$$
$$- \frac{1}{\sigma_1 (N_t, R_t N_t T)} \left[ R_t \frac{\partial (N_t T)}{\partial t} \sigma_2 (N_t, R_t N_t T) \right]$$
$$+ \frac{1}{J (R_t N_t, N_t T)} \left[ \frac{\partial (N_t T)}{\partial t} \sigma_2 (R_t N_t, N_t T) \right]$$
(5-23)

where

$$\sigma_2(e,f) = \frac{\partial}{\partial f} \left[ J(e,f) \right] = \exp(-e-f) \left(\frac{e}{f}\right)^{\frac{1}{2}} I_1(2\sqrt{ef})$$
 (5-24)

$$\frac{\partial (N_{t}T)}{\partial x} = -\frac{N_{t}T}{t'v}$$
(5-25)

$$\frac{\partial (N_{t}T)}{\partial t} = -v \frac{\partial (N_{t}T)}{\partial x} = \frac{N_{t}T}{t}$$
(5-26)

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# 5.2.2 Diffusion-controlled ligand exchange

The rate-limiting step in most sorption processes is transient diffusion through the sorbent matrix. If the sorption isotherm is linearized, analytical solutions can be used to calculate the fixed-bed response. Nonlinear sorption isotherms require numerical solutions to predict the column-effluent concentration profile. In all of these solutions, the particle-average sorbate accumulation is related to film transfer at the sorbent surface by

$$\rho_{b} \frac{\partial q_{a}}{\partial t'} = k_{f} a_{I}(C_{f} - C^{*}); r = R, t' > 0, x \ge 0$$
(5-27)

The general form of the transient diffusion equation is

$$\varepsilon_{\mathbf{p}} \frac{\partial \mathbf{C}_{\mathbf{p}}}{\partial t'} + \rho_{\mathbf{p}} \frac{\partial \mathbf{q}}{\partial t'} = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 [\varepsilon_{\mathbf{p}} \mathbf{D}_{\mathbf{p}} \frac{\partial \mathbf{C}_{\mathbf{p}}}{\partial r} + \rho_{\mathbf{p}} \mathbf{D}_{\mathbf{s}} \frac{\partial \mathbf{q}}{\partial r}]$$
(5-28)

It is subjected to the following conditions

\_ \_

$$k_{f}(C_{f} - C^{\star}) = \epsilon_{p}D_{p} \frac{\partial C_{p}}{\partial r} + \rho_{p}D_{s} \frac{\partial q}{\partial r}; r = R, t' > 0, x \ge 0 \quad (5-29)$$

$$\frac{\partial C_p}{\partial r} = \frac{\partial q}{\partial r} = 0; r = 0, t' \ge 0, x \ge 0$$
(5-30)

$$\mathbf{q} = \mathbf{f}(\mathbf{C}_{\mathbf{p}}); \ \mathbf{0} \leq \mathbf{r} \leq \mathbf{R}, \ \mathbf{t}' \geq \mathbf{0}, \ \mathbf{x} \geq \mathbf{0}$$
(5-31)

$$C_p = q = 0; 0 \le r < R, x \ge 0$$
 (5-32)

for ligand sorption and

.

$$C_{n} = C_{0}'; 0 \le r \le R, x \ge 0$$
 (5-33)

$$q = q_0'; 0 \le r < R, x \ge 0$$
 (5-34)

for column elution.

## 5.2.2.1 Linear Equilibrium

Rosen developed the solution for a linear fixed-bed sorber where the rate of sorption is determined by liquid-film and solid diffusion [94]. The solution for a linear-isotherm batch sorber (Chapter IV) suggests that the same solution form can also describe pore and combined-diffusion processes. The transient solid-diffusion equation is

$$\frac{D_{h}}{r^{2}}\frac{\partial}{\partial r}r^{2}\frac{\partial q}{\partial r} = \frac{\partial q}{\partial t'}$$
(5-35)

Using the appropriate conditions derived from equation (5-27) through equation (5-32), Rosen obtained the exact solution to this problem in form of an infinite integral. He also gave a useful approximate solution that is a function of three dimensionless parameters

$$\eta_{r} = \frac{3 \rho_{b} D_{h} K L}{\epsilon_{b} v R^{2}}$$
(5-36)

$$\phi_{\mathbf{r}} = \frac{\mathbf{k}_{\mathbf{f}} \mathbf{R} (1 - \varepsilon_{\mathbf{b}})}{\rho_{\mathbf{b}} D_{\mathbf{h}} \mathbf{K}} = \frac{\mathbf{k}_{\mathbf{f}} \mathbf{R}}{\rho_{\mathbf{p}} D_{\mathbf{h}} \mathbf{K}}$$
(5-37)

$$\theta_r = \frac{2 D_h t'}{R^2}$$
 (5-38)

Nonetheless, this solution form is a complicated relationship of hyperbolic trigonometric functions and will not be reproduced here. The approximation agrees with the infinite-integral solution [95] in the second and third digit. This comparison was performed for most of the tabulated results on the rigorous solution.

Thomas presented an earlier solution to the above problem as he recognized that intraparticle diffusion can control fixed-bed sorption rates [96]. However, his solution does not include film transfer. The form of the Rosen solution is similar to that of more complicated fixed-bed problems including finite surface kinetics [97], longitudinal dispersion [98] and both [99].

The Rosen solution can be simplified by assuming that the intraparticle concentration profile obeys an axial and time-dependent parabolic response

$$q = a_0(x,t) + a_2(x,t)r^2$$
 (5-39)

Liaw et al. [93] first solved this problem and Rice [67] presented the solution in terms of the familiar J-function :

$$\boldsymbol{v}_{f} = J(\boldsymbol{\eta}_{1}, \boldsymbol{\theta}_{1}) \tag{5-40}$$

where

$$\eta_{1} = \frac{15 \rho_{b} D_{h} K x}{R^{2} (5/\phi_{1} + 1) \varepsilon_{b} v}$$
(5-41)

$$\theta_1 = \frac{15 \ D_h t'}{R^2 (5/\phi_1 + 1)}$$
(5-42)

$$\phi_1 = \phi_r = \frac{k_f R}{\rho_p D_h K}$$
(5-43)

Because of the linearity of this problem, the column-elution response can be predicted from the previously-stated solutions for loading conditions:

$$U_{f}(elution) = 1 - U_{f}(sorption)$$
 (5-44)

When a nonlinear isotherm is used, the fixed-bed problem requires a numerical solution.

## 5.2.2.2 Nonlinear Equilibrium

The liquid-phase material balance, derived from equations (5-2) and (5-27), takes the same dimensionless form for each nonlinear model

$$\frac{\partial \mathbf{U}_{f}}{\partial \beta} + \eta \phi [\mathbf{U}_{f} - \mathbf{U}^{\star}] = 0$$
(5-45)

This equation is discretized at M axial-interior collocation points and at each exterior boundary

$$\begin{array}{l} M+1 \\ \Sigma & D_{jk} & U_{fk} + \eta \phi [U_{fj} - U_{j}^{\star}] = 0; \ 1 \leq j \leq M+1 \\ k=0 \end{array}$$
 (5-46)

The approximating polynomial for the trial-function was  $P_{M}^{(0,0)}(\beta)$ , the Legendre polynomial. Expanding the above equation, the result is

$$\begin{array}{cccc} & M+1 & & \\ \Sigma & D_{jk} & U_{fk} + [D_{jj} + \eta \phi] U_{fj} + D_{j0} U_0 - \eta \phi U_j^* = 0; \\ & & k \neq j = 1 & & \\ & 1 \leq j \leq M+1 & & \\ \end{array}$$
(5-47)

The front-face bed concentration  $U_0$  is known from the boundary condition, equation (5-3) or (5-6). The bed-voidage concentrations are initialized from the equation

$$\frac{d\upsilon_f}{d\beta} + \eta\phi[\upsilon_f - \upsilon^*] = 0$$
(5-48)

since the sorbent particles all have the same initial concentration. Thus, the initial bed-concentration profile is described by

$$\mathbf{U}_{\mathbf{f}} = \mathbf{U}^* + \left[\mathbf{U}_{\mathbf{f}} - \mathbf{U}^*\right]_{\mathbf{O}} \exp(-\eta\phi\beta) \qquad (5-49)$$

This equation is appropriate for both loading

(5-50)

72

$$v_f = \exp(-\eta\phi\beta)$$

and regeneration

$$\mathbf{U}_{\mathbf{f}} = \mathbf{1} - \exp(-\eta \phi \beta) \tag{5-51}$$

The sorbent-phase material balance, for each diffusion mechanism, is essentially the same as the corresponding batch sorber model (developed in Chapter IV). The dimensionless time and film transfer expressions were changed to accomodate the new geometry. The resulting collocation forms are presented without derivation:

# Pore Diffusion Model

$$Dep_{i} \left[ \sum_{m=1}^{N} (T_{im} - \frac{2 T_{i,N+1} \cdot A_{N+1,m}}{2 A_{N+1,N+1} + \phi_{p}}) U_{pm}^{(j)} + \frac{T_{i,N+1} \cdot \phi_{p} \cdot U_{fj}}{2 A_{N+1,N+1} + \phi_{p}} \right]$$
$$= \frac{dU_{pi}^{(j)}}{d\theta_{p}}; \quad 1 \le i \le N, \ 1 \le j \le M+1$$
(5-52)
$$Dep_{i} = \{1 + g' [U_{pi}^{(j)}]/\gamma \}^{-1}$$

$$\frac{dQ_{a}^{(j)}}{d\Theta_{p}} = \frac{5\gamma\phi_{p}}{(2A_{N+1,N+1} + \phi_{p})} \begin{bmatrix} N & (j) \\ \Sigma & A_{N+1,j} & U_{pm} \end{bmatrix}$$

$$+ A_{N+1,N+1} & U_{fj}; 1 \le j \le M+1 \qquad (5-53)$$

$$u_{j}^{*} = u_{pN+1}^{(j)} = \frac{\phi_{p}}{(\phi_{p} + 2A_{N+1,N+1})} \left[ u_{fj} - \frac{2}{\phi_{p}} \prod_{m=1}^{N} A_{N+1,m} u_{pm}^{(j)} \right]; 1 \le j \le M+1$$
(5-54)

$$\eta_{\mathbf{p}} = \frac{3(1 - \epsilon_{\mathbf{b}}) \mathbf{L} \epsilon_{\mathbf{p}} \mathbf{D}_{\mathbf{p}}}{\epsilon_{\mathbf{b}} \mathbf{v} \mathbf{R}^2}$$
(5-55)

$$\phi_{\mathbf{p}} = \frac{\mathbf{k}_{\mathbf{f}}^{\mathbf{R}}}{\varepsilon_{\mathbf{p}}^{\mathbf{D}_{\mathbf{p}}}} \tag{5-56}$$

Solid Diffusion Model

.

$$\frac{dQ_{i}^{(j)}}{d\theta_{h}} = \sum_{m=1}^{N+1} T_{im} Q_{m}^{(j)}; 1 \le i \le N, 1 \le j \le M+1$$
 (5-57)

$$\psi \frac{dQ_{N+1}^{(j)}}{d\theta_{h}} = \alpha U_{fj} + 2[(\alpha-1)Q_{N+1}^{(j)} - \alpha] \begin{bmatrix} N \\ \Sigma \\ m=1 \end{bmatrix} A_{N+1,m} Q_{m}^{(j)} ]/\phi_{h}$$

$$- Q_{N+1}^{(j)} [2\alpha A_{N+1,N+1}/\phi_{h} + 1 + (\alpha - 1)U_{fj}]$$

$$+ 2(\alpha - 1) A_{N+1,N+1} [Q_{N+1}^{(j)}]^{2}/\phi_{h}; \quad 1 \le j \le M+1$$
(5-58)

$$\frac{dQ_a^{(j)}}{d\theta_h} = 6 \sum_{m=1}^{N+1} A_{N+1,m} Q_m^{(j)}; 1 \le j \le M+1$$
(5-59)

$$U_{j}^{*} = U_{fj} - \frac{2}{\phi_{h}} \sum_{m=1}^{N+1} A_{N+1,m} Q_{m}^{(j)}; 1 \le j \le M+1$$
 (5-60)

,

$$\eta_{h} = \frac{3 L \rho_{b} D_{h} q_{0}}{\varepsilon_{b} v R^{2} C_{0}} = \frac{3(1 - \varepsilon_{b}) L \varepsilon_{p} D_{h}}{\gamma \varepsilon_{b} v R^{2}}$$
(5-61)

$$\phi_{h} = \frac{k_{f}(1 - \varepsilon_{h}) C_{0} R}{\rho_{h} D_{h} q_{0}} = \frac{k_{f} \gamma R}{\varepsilon_{p} D_{h}}$$
(5-62)

.

The numerical solution was performed for each model as follows:

- Use equation (5-49) to initialize the bed-concentration profile.
- 2. With the appropriate bed-void concentration, solve the sorbent-phase material balance at each bed position j to get the fluid-side interfacial concentration Uj\*. The ODEs are integrated over a small-enough time step to assume the bed concentration profile constant.
- 3. The array of interfacial concentrations is used to solve the liquid-phase material balance, equation (5-47), by Gaussian elimination.
- 4. The second and third steps are repeated for successive dimensionless-time increments until the bed-effluent concentration adequately approaches the feed concentration.

Similar numerical techniques have been presented by other authors in modelling fixed-bed adsorbers. Raghavan and Ruthven [100] illustrated the application of orthogonal collocation to a linear fixed-bed problem with axial dispersion. Liapis and Rippin [101] used the same technique to solve a binary-adsorption, pore-diffusion model with axial dispersion. Also, the solid diffusion model has been used to simulate many different fixed-bed adsorption systems [75,102]. Crittenden et al. [103] used the method of orthogonal collocation to simulate multicomponent adsorption with solid diffusion. To avoid difficulties in solving the transient-diffusion collocation equations, they used quadrature to determine the average sorbent concentration at each bed position (a recognized overstatement of the problem). Some difficulty was probably caused by the nonlinear boundary condition, multicomponent Langmuir equilibrium at the sorbent-particle boundary.

The present solution scheme involves the solution of M+1 simultaneous equations for the liquid-phase material balance pore diffusion in each model. The model requires (M+1)x(N+1)ODEs to be integrated in solving the sorbent-phase material balance. Ligand sorbent-phase transients in the solid diffusion model are represented by (M+1)x(N+2) differential equations. The solution of a differential-algebraic system is avoided by 1) converting the nonlinear boundary condition into an "ultra-stiff" ODE (deveolped for the the solid-diffusion model in Chapter IV) and 2) assuming the bed-concentration profile does not change over a small time step. Because of the oscillating nature of the orthogonal-polynomial approximation, an initially suppress attempt was made to unnecessary integration the spherical-diffusion of collocation The driving force for ligand transfer should be equations. initially insignificant near the exit of a long (large  $\eta$ ) Thus, when the film-transfer concentration exchange bed. difference was greater than 10<sup>-4</sup>, the sorbent-phase ODEs

were solved at that particular bed position. Otherwise, the sorbent-phase material balance was not solved and this re-initialized. concentration profile was The average-sorbent concentration was also calculated at each bed position to show the approach to constant-pattern conditions [104,105]. The film transfer coefficients were determined from correlations proposed by Wilson et al. [106] and Kataoka et al. [107]. This numerical technique was verified by comparison with the approximate Rosen solution [94]. The column-effluent concentrations were comparable in the second and third digits at dimensionless times greater than  $3 \times 10^{-2}$  (see Table 4).

-----

Table 4: Numerical Solution of the Rosen Problem

Dimensionless Time Step =  $2 \times 10^{-5}$ Bed Length Parameter = 0.90 Film Resistance Parameter = 44.4 Number of Radial-interior Collocation Points N = 8 Number of Axial-interior Collocation Points M = 8

Time	Unitless Bed-effluent Concentration			
	Rosen Model	Numerical Solution		
1x10-2	6.11x10 <sup>-5</sup>	1.16x10-4		
2x10 <sup>-2</sup>	1.25x10-3	1.24x10 <sup>-3</sup>		
3x10-2	5.63x10-3	5.49x10-3		
4x10-2	1.43x10 <sup>-2</sup>	1.40x10 <sup>-2</sup>		
5x10-2	2.74x10 <sup>-2</sup>	2.69x10-2		
7x10-2	6.40x10 <sup>-2</sup>	6.34x10 <sup>-2</sup>		
1x10 <sup>-1</sup>	1.35x10-1	1.34x10 <sup>-1</sup>		
1.5x10-1	2.65x10 <sup>-1</sup>	2.64x10 <sup>-1</sup>		
2x10~1	3.89x10 <sup>-1</sup>	3.88x10 <sup>-1</sup>		
2.5x10-1	5.01x10 <sup>-1</sup>	4.99x10 <sup>-1</sup>		
3x10-1	5.97x10-1	5.94x10 <sup>-1</sup>		
3.5x10-1	6.77x10 <sup>-1</sup>	6.75x10 <sup>-1</sup>		
4x10 <sup>-1</sup>	7.43x10 <sup>-1</sup>	7.42x10+1		
4.5x10 <sup>-1</sup>	7.96x10 <sup>-1</sup>	7.97x10 <sup>-1</sup>		
5x10-1	8.37x10 <sup>-1</sup>	8.42x10 <sup>-1</sup>		
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#### Chapter VI

#### EVALUATION OF EXPERIMENTAL RESULTS

The batch experimental data were analyzed to obtain Langmuir isotherm parameters and diffusion coefficients. These model parameters were used to estimate column-effluent concentration profiles for ligand exchange beds. The results on fixed-bed regeneration were also evaluated. The experimental data are shown in Appendix C.

## 6.1 Model Parameter Assessment

The ligand-sorption equilibria agree with the theoretical presumptions of Helfferich. Sorbent-phase diffusivities obtained for the amines show that surface diffusion does not significantly contribute to intraparticle mass transfer.

## 6.1.1 Langmuir Models

The equilibrium curve for butylamine (BA) at 22°C has been previously shown in Figure 7. Diglycolamine (DGA) isotherms at 22°C and 50°C are presented in Figure 10 and Figure 11, respectively. The appropriate Langmuir parameters are given in Table 5. The 95% joint confidence region is defined for each of the Langmuir parameter pairs in Figures 9, 12 and 13.



Figure 10: Diglycolamine Equilibrium at 22°C



Figure 11: Diglycolamine Equilibrium at 50°C



Figure 12: The 95% Joint Confidence Region for DGA Langmuir Parameters at 22°C



Figure 13: The 95% Joint Confidence Region for DGA Langmuir Parameters at 50°C

Isotherm	a (L soln/g resin)	b (L soln/mg)	g <sub>m</sub> = a/b ★
BA at 22 <i>°</i> C	4.16	1.14x10 <sup>~2</sup>	366 (5.0)
DGA at 22°C	2.21	1.04x10 <sup>~2</sup>	212 (2.0)
DGA at 50°C	7.83	1.64x10 <sup>-1</sup>	47.8 (0.45)

Table 5: Langmuir Equilibrium Parameters

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\* parenthetical values are in meg/g resin

There appears to be a significant amount of data scatter about the Langmuir-predicted trend. This error is reflected in the relative size of the confidence regions. Some explanation for these inaccuracies can be given:

- Titration errors (±1 to 2 mg/L) have the most serious effect at the lower and upper concentrations of the equilibrium relationship.
- Variable copper content of the resin could also be a source of error. Even though the copper loading was found to agree with the resin ion-exchange capacity, random differences in this amount could exist among individual samples (since they were prepared independently).

Nevertheless, with respect to these inherent errors, the Langmuir approximation adequately represents the ligand exchange equilibria.

The nature of this experimental data corresponds with the theoretical presumptions of Helfferich [22]. Each of the isotherms exhibit a downward concavity. The DGA isotherms (Figures 10 and 11) show that the complex formation is favorable at low temperatures. The sorbent capacity for DGA decreases over 75% with a 30°C temperature rise. Thus, DGA recovery seems possible with low-temperature sorption and fixed-bed operation. high-temperature elution in а Helfferich also noted that, if complexation is strong, the ligand content approximately equals the ligand-exchange capacity over a wide range of the external solution From the information in Table 5 and the concentration. corresponding figures, the amine ligand complexes are apparently not strong. This result agrees with tabulated instability constants for methylamine [20, p.145]. The ligand-exchange capacity of this copper-loaded, carboxylic acid resin is about 10 meq/g resin ( $X_1 = 5.2, z_m = 2, N_m =$ 4). The Langmuir maximum sorbent capacity q, falls short of this value for both of the amines at 22°C (the exchange column data show this value to be slightly higher for DGA). One reason for this incomplete complexation is steric hindrance to the coordinate covalent bond. The structure of butylamine

and diglycolamine

Н	н	Н	Н	
1	1	1		
H-0-C-	•C-(	0-Ċ-	٠ċ٠	-N-H
1	T.	1	ł	1
н	Ĥ	Ĥ	Ĥ	Ĥ

suggests that the coordination sites of the copper are blocked from the amine-nitrogen electron pairs by aliphatic groups. This same effect is chemically modelled in "hindered amines" for the selective removal of acid gas components (see Chapter I). Also, DGA has alcohol and ether oxygens that may contribute electron pairs to occupy the copper coordination valences (making it a bidentate or tridentate chelate). In any case, the capacities are large enough to suggest advantages over non-specific sorption processes such as physical adsorption or ion exchange.

# 6.1.2 Diffusion Coefficients

The accuracy of the spectrophotometric method is very important in the interpretation of batch sorber data. A response curve (with duplicate samples) for butylamine was previously shown in Figure 5. The results of another spectrophotometric test for diglycolamine are given in Figure 14. The analytical-test model parameters are reported in Table 6. The correlation coefficients (close to 1) show that a modified Beer's Law model calibrates the amine-test standards very well. The parameter confidence intervals also indicate the accuracy of this analytical technique.

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<u>Table 6</u> : Amine Test Model Parameters				
Amine	Model Results     log(fractional transmittance) = Z <sub>1</sub> + Z <sub>2</sub> C			
	Z <sub>1</sub> *	Z2*   (L soln/mg)	Correlation Coefficient	
. <b>BA</b>	-0.0734 ±0.0039	-0.00256 ±0.00032	0.988	
DGA	-0.0672   ±0.0051	-0.00282 ±0.00047	0.973	
<u> </u>	I	·····		

\* error values indicate 95% confidence intervals

After a batch sorption run, the data were interpreted by performing this analytical technique on the samples and standards in the same test procedure.

The ambient batch sorber runs were mathematically modelled as previously described in Chapter IV. Some results for the pore diffusion model are given in Table 7 for both BA and DGA (other run information for for the given codes is shown in Appendix C). The results are illustrated



# <u>Figure 14</u>: Spectrophotometric Determination of Diglycolamine

in Figures 15 through 17. Film transfer coefficients were obtained from equation (4-51) using the first few data pairs These values give suspiciously high in each run. They were used in mathematical modelling of diffusivities. fixed-bed responses and found in disagreement with experimental results. The first few data points in a sorber response may not be useful if mixing is initially incomplete. Hence, many researchers choose experimental conditions that minimize film resistance in batch sorption processes [56,57,67]. By increasing the agitation speed of the sorber bath, the film transfer coefficient becomes large enough to virtually eliminate any difference between the sorber solution and interfacial concentrations. These simplifications are easily incorporated into the model developments of Chapter IV. The modelling results for this case, pore diffusion without film resistance, are also given These simulations are shown in Figures 18 in Table 7. The unitless time scale was defined in the through 23. Chapter IV model development. An increase in the impeller speed does give an increase in the observed diffusivity (film resistance is still contributing to the mass transfer process). However, the difference is small when compared to the accuracy of this determination ( a 5% increase in S is bounded by a 10 - 15% error in the optimum diffusion Because of the possibility of sorbent coefficient). breakup, the batch mixing speed was not increased further.

Run Code	Mixing   Speed   (rpm)	kf (cm/sec)	Film  Transfer  Included	Optimum D <sub>P</sub> (cm <sup>2</sup> /sec)	Optimum D <sub>h</sub> (cm²/sec)
BA2	500	0.00353	   ¥ES	4.0x10 <sup>-5</sup>	
BA3	600	0.00551	YES	3.7x10-5	
DGA1	600	0.00694	YES	3.7x10 <sup>-5</sup>	
BA1	600	0.00447	NO	5.0x10 <sup>-6</sup>	1.9x10 <sup>-9</sup>
BA2	500	0.00353	NO	3.5x10 <sup>-6</sup>	<sup>·</sup> 1.8x10 <sup>-9</sup>
BA3	600	0.00551	NO	5.4x10 <sup>-6</sup>	2.5x10-9
DGA1	600	0.00694	NO	6.9x10-6	3.7x10 <sup>-9</sup>
DGA2	600	0.00397	NO	5.2x10 <sup>-6</sup>	2.5x10-9
DGA3	600	0.00646	NO	6.9x10-6	3.8x10-9
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#### Table 7: Batch Sorber Results

Apparent sorbent density0.55 g/cm³Sorbent porosity0.38Sorbent particle radius0.03 cmBatch sorber volume1000 cm³

There is some disagreement in the model fit at larger dimensionless times. This is undoubtedly a result of the "no-film resistance" approximation. The DGA-isotherm sorbent capacities were obviously low in comparison with estimations from the fixed-bed responses (see the next section). And, since the DGA sorber runs were all performed with an initial concentration at about 160 mg/L, the















Figure 18: Butylamine (BA1) Batch Sorber - Pore Diffusion


Figure 19: Butylamine (BA2) Batch Sorber - Pore Diffusion



Figure 20: Butylamine (BA3) Batch Sorber - Pore Diffusion



<u>Figure 21</u>: Diglycolamine (DGA1) Batch Sorber - Pore Diffusion



<u>Figure 22</u>: Diglycolamine (DGA2) Diffusion

Batch Sorber - Pore



<u>Figure 23</u>: Diglycolamine (DGA3) Batch Sorber - Pore Diffusion

DGA-equilibrium sorbent capacity used in these simulations was 190 mg/g. Otherwise, the determination of intraparticle diffusivities would incorporate some of the isotherm parameter imprecision [103]. In any case, the batch equilibrium parameters give a good representation of the isotherm curvature.

The model fit also deviates from the experimental sorber profiles in the time-scale intermediate region. Although some of this deviation may be attributed to analytical error, the consistency of the disagreement (for all batch sorber profiles of both amines) suggests a misrepresentation in the mathematical modelling. Qualitatively, ligand saturation of the coordinative valences appears to occur in more than one "stage." Thus, the model-data discrepancy may be avoided by using the theoretical isotherm model given by Helfferich (see Chapter IV). Nevertheless, the simplicity of the Langmuir approximation justifies its usage.

The contribution of film resistance can be ascertained from a single-resistance model [76]. This simulation is represented by assuming a very large diffusivity ( $D_p = 0.1$  $cm^2/sec$ ) associated with the calculated film transfer coefficient (thereby depicting a radially invariant sorbent-concentration profile). Results for this model (assuming pore diffusion transport) are given in Figures 24 and 25 for BA and DGA, respectively. From these graphs, it is concluded that intraparticle diffusion dominates over

most of the batch sorber time scale. Weber et al. [76] also note that a batch sorber response is very sensitive to deviations in the mass transfer coefficient when the solid-to-liquid phase solute distribution is high. Thus, the neglect of film resistance gives a very useful first-approximation to these intraparticle diffusivities.

The results show that pore diffusion is the dominant intraparticle diffusion mechanism. The molecular diffusion coefficients at 22°C are 8.3x10<sup>-6</sup> and 7.6x10<sup>-6</sup> cm<sup>2</sup>/sec for BA and DGA, respectively. The pore diffusivities determined in this work are less than the corresponding molecular diffusivities. A representative tortuosity could be obtained for this sorbent with an experimental diffusion coefficient measured in the sorber concentration range [82]. [108] and Costa et al. [109] give pore Erickson et al. diffusivities of similar magnitude in ion exchange resins. The solid diffusion model does not presume surface diffusion to be the only intraparticle diffusion mechanism. Therefore, solid diffusivities were also estimated from the batch data. These values, tallied in Table 7, are depicted in Figures 26 through 31. The values for butylamine agree with the semi-empirical estimate of Groves [36]. The solid diffusion model also gives a reasonable fit to the data. Again, as with the pore diffusion model, this model does not adequately conform to the data at intermediate and large This discrepancy must be accepted as the sacrifice times.



Figure 24: Butylamine (BA3) Batch Sorber - Film Diffusion





Diglycolamine (DGA1) Diffusion

Batch Sorber

- Film

for convenient approximations. Nevertheless, the observed diffusion coefficients give the best representation of all of the experimental data - batch sorption and fixed bed.



Figure 26: Butylamine (BA1) Batch Sorber - Solid Diffusion



Figure 27: Butylamine (BA2) Batch Sorber - Solid Diffusion



Figure 28: Butylamine (BA3) Batch Sorber - Solid Diffusion



<u>Figure 29</u>: Diglycolamine (DGA1) Batch Sorber - Solid Diffusion

.







<u>Figure 31</u>: Diglycolamine (DGA3) Batch Sorber - Solid Diffusion

#### 6.2 Exchange Column Data

The results from fixed-bed, ligand-sorption columns are discussed and the responses are mathematically modelled. Also, the regeneration column data are qualitatively rated.

### 6.2.1 Discussion of Sorption Runs

Information on the ligand sorption runs is presented in Table 8 (the data for these run codes is given in more complete form in Appendix C). The effluent concentration profiles, shown in Figures 32 through 39, include results for BA, DGA and TEA (triethylamine). Another alkanolamine, 2-amino-2-methyl-1-propanol, was used as feed for a fixed-bed sorption column. This amine displaced the copper from the resin during the loading run. No further experimentation was performed with this ligand since the chosen metal-resin sorbent could not effectively chemisorb For most of these loading curves, the fixed-bed column it. was not long enough to contain the "S"-shaped wavefront. These exchange columns, classified as microcolumns or short-bed sorbers, might be sensitive to the diffusivity and film transfer used in modelling the profiles [59-61]. Even though the column flowrates ranged from about 1 to 2 ml/min, the loading runs never took less than 200 bed volumes to breakthrough. Equilibrium and end-of-run sorbent capacities were estimated from appropriate areas on the bed-effluent concentration profile. This graphical material balance is illustrated in Figure 40.

Run Cođe	C <sub>ø</sub> (mg/L)	q at end of run (mg/g)	Column predicted q <sub>0</sub> (mg/g)	Batch Studies q <sub>0</sub> (mg/g)	Break- through** (bed volumes)
BAL1	223	150	200	262	220
BAL2	195	170	230	252	310
BAL3*	190	210	300	250	290
DGAL1	164	99		134	210
DGAL2	164	182	190	134	480
DGAL3	178	180	200	138	230
DGAL4*	162	87		133	300
TEA*	167	96			280

## Table 8: Column Sorption Data

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\* Column diameter 1.08 cm
\*\* Breakthrough is defined as the bed-volume throughput required to raise the effluent concentration to 20% of the feed. . • •

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Figure 32: Butylamine (BAL1) Sorption Column Response



Figure 33: Butylamine (BAL2) Sorption Column Response



Figure 34: Butylamine (BAL3) Sorption Column Response



Figure 35: Diglycolamine (DGAL1) Sorption Column Response



Figure 36: Diglycolamine (DGAL2) Sorption Column Response







Figure 38: Diglycolamine (DGAL4) Sorption Column Response



Figure 39: Triethylamine (TEA) Sorption Column Response





## 6.2.2 Modelling Results

The column ligand sorption profiles were predicted with numerical and Thomas-model simulators. All of these models were generally predictive of the column response.

#### 6.2.2.1 Numerical Simulators

The ligand-sorption column responses were simulated with the previously derived model parameters. The DGA sorbent capacities were again adjusted (as for the batch sorber modelling) to agree with the column-sorption material balance. This procedure is not unusual [103]. The pore and solid-diffusion models were used to numerically simulate the fixed-bed loading curves. The optimum numerical parameters are given in Table 9. These values gave convergence within the second to third digit of the effluent-concentration The Wilson et al. correlation [106] was used to profile. estimate the film transfer coefficient; the values obtained were about the same as those from the Kataoka et al. [107] correlation. Other parameters for the loading run simulations are given in Table 10. The simulations are displayed in Figures 41 through 47 for the pore diffusion model. The solid-diffusion model predictions are graphed in Figures 48 through 54. On each of these graphs, the abscissa is the unitless time which corresponds to the given model (derived in Chapter V). The sensitivity of these model responses is illustrated in Figures 55 through 58. Both models have essentially the same sensitivity to changes

in the film transfer coefficient. However, the pore diffusion model is much more sensitive to a change in its diffusivity than the solid diffusion model; this evidence supports the pore-diffusion transport mechanism. The pore diffusivity also affects the sorbent capacity (obtained from the column material balance). This result was also discovered for the batch sorption responses (in the previous section).

Parameter	Pore Diffusion Model	Solid Diffusion Model
Radial-interior Collocation Points	4	4
Axial-interior Collocation Points	6	6
Unitless time step	5x10-2	5x10 <sup>-5</sup>
Stiffness factor		10-5
DGA Diffusivity	6.9x10 <sup>-6</sup>	3.8x10 <sup>~9</sup>
BA Diffusivity	5.4x10 <sup>-6</sup>	2.5x10 <sup>-9</sup>
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Table 9: Numerical Simulation Parameters

Bulk-bed density0.35 g/cm³Particle density0.55 g/cm³Bed voidage0.36Fluid density1.0 g/cm³Fluid viscosity1.0 cPD (DGA)7.6x10<sup>-6</sup> cm²/secD (BA)8.3x10<sup>-6</sup> cm²/sec

Run Cođe	C <sub>0</sub>	Sorbent Weight	9.0 P	ε <sub>Ϸ</sub> ν	k <sub>⊈</sub>
	(mg/L)	(g)	(mg/g) <sup>.</sup>	(cm/s)	(cm/s)
BAL1	223	2.00	262	0.034	0.0026
BAL2	195	1.93	252	0.038	0.0027
BAL3	190	2.03	250	0.020	0.0022
DGAL1	164	2.36	190*	0.057	0.0030
DGAL2	164	2.38	190*	0.029	0.0024
DGAL3	178	1.48	200*	0.043	0.0027
DGAL4	162	2.01	190*	0.028	0.0024

## Table 10: Sorption-Column Run Parameters

\* Adjusted to agree with column material balance

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There are noticeable discrepancies in the model-data agreement for both amine model simulators. They are initial bed breakthrough, data scatter and material balance disagreement. Explanations for these errors can be summarized as follows:

 Flowrate. The feed was not consistent throughout the sorption run. Sorbent swelling (with ligand uptake) is a probable cause of this error. This parameter, very important in the short-bed adsorber analysis [59-61], could cause variation in the initial and final portions



















# <u>Figure 45</u>: Diglycolamine (DGAL2) Sorption Column - Pore Diffusion Model



<u>Figure 46</u>: Diglycolamine (DGAL3) Sorption Column - Pore Diffusion Model


<u>Figure 47</u>: Diglycolamine (DGAL4) Sorption Column - Pore Diffusion Model



<u>Figure 48</u>: Butylamine (BAL1) Sorption Column - Solid Diffusion Model









.



<u>Figure 51</u>: Diglycolamine (DGAL1) Sorption Column - Solid Diffusion Model





Sorption Column - Solid











Figure 55: Pore Diffusion Model Sensitivity to kf - Run BAL1



<u>Figure 56</u>: Pore Diffusion Model Sensitivity to  $D_{\mathbf{p}}$  - Run BAL1



<u>Figure 57</u>: Solid Diffusion Model Sensitivity to k<sub>f</sub> - Run BAL1



<u>Figure 58</u>: Solid Diffusion Model Sensitivity to D<sub>6</sub> - Run BAL1

of the loading curves. This also causes an inconsistent evaluation of the film transfer coefficient, affecting the initial bed-effluent concentrations.

- Dispersion. Although ruled out for similar work [59-61], axial dispersion might have an influence on the column-effluent concentration profile. Liapis and Rippin [101] include the effect of axial dispersion for their multicomponent system. Their bed-particle diameter ratio was about 50 and the particle Reynolds number about 1.6. In this work, the bed-particle diameter ratios were 14 and 18 (the particle diameter was 0.06 cm and the bed diameters were 0.84 and 1.08 cm). The particle Reynolds number ranged from 0.1 to 0.2. Runs in the two different column diameters (with similar operating conditions showed no significant difference in the nature of the response. However, even at these slow velocities, wall effects could have influenced the column-effluent profile [110].
- Isotherm inconsistencies. Sorbent capacities predicted from the isotherm were much lower than those observed in the DGA loading runs. This error may have been caused by a) incomplete data within the loading concentration range and/or b) insufficient equilibration time for batch experiments. Nonetheless, the capacities predicted from the column-sorption material balance can be no more than 80 to 90% accurate. They depend on the

full development of the concentration profile (final bed-effluent concentrations should be close to that of the feed to get good accuracy on the extrapolation). This error causes disagreement in the material balance. Also, the Langmuir isotherm approximation may not be an appropriate representation of the equilibrium. This could affect the shape of the fixed-bed profile at the initial and final stages.

 Film-transfer coefficient errors. This value has been found to be in error by 20 to 30% or more [61,101]. A decrease in this parameter would be required to strengthen the model-data agreement for the initial portion of the concentration profile. This error could also affect the steepness of the response in the intermediate region.

All things considered, the numerical simulators were generally predictive of the column response. The solid diffusion simulations required 6 to 8 cpu minutes on an IBM 3084 computer to predict the entire effluent profile. The pore diffusion model only required 2 to 4 cpu minutes to simulate the column response. These results suggest an extension of the techinique for multicomponent ligand exchange.

# 6.2.2.2 Thomas Models

The Thomas models were also used to simulate the ligand Model parameters used in these predictions were sorption. taken from the solid diffusion simulations. The relationship of equations (4-6) and (5-11) allowed correct interpretation of the model parameters. The results, for both kinetic driving forces, are given in Figures 59 through 72. These graphs show that the Thomas model can also be used to predict ligand-sorption column profiles. Some of the inaccuracies of this solution can be related to the estimation of the net sorption rate (see Chapter V). kinetic parameter is determined Recall, the from a constant-pattern assumption. The numerical simulators, which calculate  $Q_a$  and  $U_a$  at each bed position, show that these conditions do not exist for the column runs in this Nevertheless, this model does a reasonable job at work. fitting the data (since the parameters were obtained from the fundamental, solid-diffusion model). For single sorbate systems with deep beds, the Thomas model may substitute for the solid diffusion model to give similar predictive capability with less computational effort (only a few cpu seconds are required for the estimation of a bed-effluent concentration history).



Figure 59: Butylamine (BAL1) Sorption Column - Thomas Model (5-9)



Figure 60: Butylamine (BAL2) Sorption Column - Thomas Model (5-9)



Figure 61: Butylamine (BAL3) Sorption Column - Thomas Model (5-9)



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Figure 62: Diglycolamine (DGAL1) Sorption Column - Thomas Model (5-9)



Figure 63: Diglycolamine (DGAL2) Sorption Column - Thomas Model (5-9)



Figure 64: Diglycolamine (DGAL3) Sorption Column - Thomas Model (5-9)



Figure 65: Diglycolamine (DGAL4) Sorption Column - Thomas Model (5-9)



Figure 66: Butylamine (BAL1) Sorption Column - Thomas Model (5-10)



Figure 67: Butylamine (BAL2) Sorption Column - Thomas Model (5-10)

.



Figure 68: Butylamine (BAL3) Sorption Column - Thomas Model (5-10)



Figure 69: Diglycolamine (DGAL1) Sorption Column - Thomas Model (5-10)



Figure 70: Diglycolamine (DGAL2) Sorption Column - Thomas Model (5-10)



Figure 71: Diglycolamine (DGAL3) Sorption Column - Thomas Model (5-10)



Figure 72: Diglycolamine (DGAL4) Sorption Column - Thomas Model (5-10)

## 6.2.3 Column Regeneration Performance

Some of the DGA columns were regenerated and the results are shown in Figures 73 through 75. Key information for these. runs is given in Table 11. As previously stated in Chapter III, bubble formation caused flow-channeling in the column allowing only a qualitative appraisal of the data. This incidence could have been hindered by boiling the water for all aqueous feed solutions (sorption and regeneration) and capping the feed reservoirs with an activated carbon standpipe. The carbon-filled breathing tube would adsorb much of the remaining CO<sub>2</sub> in the feed-bottle air spaces. In it is clear that the elutant wave does not Figure 73, contact the entire column cross-section. The effluent concentration never exceeds the loading feed concentration. However, when the flowrate is decreased by half (as shown in Figure 74), the regeneration profile gives a significant concentration "spike." A similar response is observed in Figure 75, where the sorption feed concentration is higher. The regeneration time-scale appears to be shorter than that of the corresponding sorption process. The other lesser peaks in the elution column profile are probably a result of channeling. Hot water, at temperatures of 50 to 60°C, does not appear to be a useful regenerant. Even with the above operational aids, a concentration increase of only two to three-fold can be expected. All of these regeneration responses can be enhanced by

- Increasing bed heat-up time. If the bed-void solution is allowed to equilibrate with the sorbent at the elevated temperature, the elution spike can be increased and the time scale decreased.
- Decreasing the flowrate. This would obviously minimize dilution of the eluted ligand.
- Increasing the temperature. As shown in the discussion ٠ of DGA equilibrium data, ligand sorption is unfavorable at high temperatures. Regeneration temperatures of 80 to 90°C may show adequate recovery of these amines.

Low-pressure steam has been proven effective as a regenerant [32,33]. This elutant should also be tried for the present ligand exchange system. However, consideration should be given to the thermal and mechanical stability of the exchange sorbent for repeated cyclic usage.


### Table 11: Column Regeneration Data

Run Code	Tempera-   ture     (°C)	Flowrate     (ml/min)	Loading   Feed  Concentration   (mg/L)	Highest Effluent Concentration (mg/L)
DGAR1	52	2.0	164	129
DGAR2	52	1.2	1 164	363
DGAR3	62	1.6	   178	419
	I	1	1	l 



Figure 73: Diglycolamine (DGAR1) Column Regeneration



Figure 74: Diglycolamine (DGAR2) Column Regeneration



Figure 75: Diglycolamine (DGAR3) Column Regeneration

#### Chapter VII

#### CONCLUSIONS AND RECOMMENDATIONS

Ligand exchange is an operationally feasible process for the removal of aqueous amines. A general research program has been defined to evaluate the prospects of a particular sorbate-sorbent system in terms of quantitative fundamental and semi-empirical analysis.

This program was successfully implemented to study the removal of butylamine and diglycolamine from aqueous streams. Copper(II)-carboxylic acid resin was found to be a suitable exchange sorbent. The ligand sorption processes were found to be mass-transfer controlled with pore diffusion dominating the mechanism. Model parameters, derived from batch experiments, were used to successfully correlate fixed-bed amine sorbers with analytical and numerical simulators.

The Thomas equations can forecast sorption-column responses but have inherent limitations for general Rigorous computer models were developed to application. fundamentally account for the nonlinear isotherm. Model equations were developed to describe batch sorption and fixed-bed columns. Film and intraparticle diffusion were included in the mathematical developments. The resulting

model equations were solved by orthogonal collocation. This numerical technique was verified by accurate prediction of the corresponding linear-isotherm analytical solutions. The usefulness of this numerical method can be extended to similar processes that do not have kinetic limitations.

Ligand-sorption column regeneration was preliminarily studied. While qualitatively evaluating ligand elution conditions, hot water was not found to be a useful regenerant for loaded fixed-bed columns.

Some recommendations for future work are:

- Further experimentation on fixed-bed regeneration. A quantitative assessment of regeneration conditions should be performed to confidently estimate ligand recovery potential.
- Economic evaluation of the sorbate-sorbent system.
  This process should be substantiated for industrial-scale operation with respect to existing water treatment facilities.
- 3. Extension of the predictive technique. It may prove useful to include axial dispersion in the fixed-bed models. Thus, the numerical simulation would have increased utility. Ligand-sorption equilibria should be modelled with the theoretical isotherm equations. The model equations can also be elaborated to account for multicomponent ligand exchange, a more realistic application.
## NOMENCLATURE

a	equilibrium parameter in equations (4-3) and				
	(4-4); in Langmuir equation (4-5), cm <sup>3</sup> soln/g				
	resin or L soln/g resin				
aI	$3(1 - \epsilon_b)/R$ , sorbent-phase interfacial area per				
	unit bed volume, cm <sup>-1</sup>				
A <sub>N+1,j</sub>	surface gradient operator for z coordinate				
А <sub>р</sub>	total sorbent surface area, cm <sup>2</sup>				
b	equilibrium parameter in equations (4-3) and				
	(4-4); in Langmuir equation (4-5), cm <sup>3</sup> soln/mg or				
	L soln/mg				
В	contour which bounds the (1-H)x100% joint				
	confidence region in equation (4-7)				
С	ligand solution concentration, mg/cm <sup>3</sup> or mg/L				
C*	sorbent-solution interfacial concentration, mg/cm <sup>3</sup>				
c <sub>o</sub>	reference solution concentration; initial sorber				
	concentration, bed-entrance concentration for				
	column loading, initial bed concentration for				
	column regeneration, mg/cm <sup>3</sup>				
с <sub>ъ</sub>	batch sorber concentration, mg/cm <sup>3</sup>				
c <sub>f</sub>	fixed-bed void concentration, mg/cm <sup>3</sup>				
с <sub>р</sub>	sorbent pore concentration, mg/cm <sup>3</sup>				
d	equilibrium parameter in equation (4-2)				
D	molecular diffusion coefficient, cm <sup>2</sup> /sec				

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- D<sub>e</sub> effective pore diffusivity, cm<sup>2</sup>/sec
- D<sub>h</sub> pseudo-homogeneous solid diffusivity defined in equation (4-36), cm<sup>2</sup>/sec
- $D_{ii}$ , gradient matrix for  $\beta$  coordinate
- pp pore diffusivity, cm<sup>2</sup>/sec
- D<sub>g</sub> surface diffusivity, cm<sup>2</sup>/sec
- D<sub>+</sub> total diffusivity defined in Table 2, cm<sup>2</sup>/sec
- $E(R_{t}, N_{t}, T, U_{f})$

objective function to be minimized in Thomas model fixed-bed design, given in equation (5-21)

- F<sub>H</sub>(i,j) that number which is exceeded with probability (1-H) by an F-distributed quantity with i and j degrees of freedom in the numerator and denominator, respecitively
- Fr restrictivity factor in equation (4-9) ranging
   from 0 to 1
- g(U) dimensionless Langmuir-type expression defined in equation (4-27)
- g'(U) first derivative of g(U) given in equation (4-27)
  G argument parameter for exponential in equation
  (5-16); defined in equation (5-17) and (5-20) for
  column loading and regeneration, respectively
- H parameter defining joint confidence region for nonlinear model parameters
- I number of terms needed to approximate J-function infinite series with minimum error, defined in equation (5-15)

J	radial mass flux, mg/(cm²·sec)			
J(e,f)	J-function defined in equations (5-12) and (5-14)			
k <sub>f</sub>	film transfer coefficient, cm/sec			
К	linear equilibrium constant, cm <sup>3</sup> soln/g resin			
к <sub>i</sub>	cumulative Bjerrum stability constant for complex			
	with ligand number i			
ĸ <sub>L</sub>	Langmuir constant defined in equation (5-11)			
L	length of fixed-bed column, cm			
<sup>m</sup> l	molality of ligand in solution phase, gmoles/kg			
	H <sub>2</sub> O ·			
м	number of axial-interior collocation points			
Ml	molality of ligand in sorbent phase, gmoles/kg H <sub>2</sub> O			
M <sub>m</sub>	molality of metal in sorbent phase, gmoles/kg $H_2O$			
Mr	mass of exchange sorbent in H+ form, g			
n	number of solute species in equation (4-3); number			
	of experimental observations in equation (4-7)			
N	number of radial-interior collocation points			
Nm	metal ion coordinative valence			
Nt	number of transfer units in Thomas model defined			
	in Table 3			
NtI	Thomas-model unitless time defined in Table 3			
P	number of model parameters in equation (4-7)			
Р	maximum ligand number for metal ion			
$P_{M}^{(0,0)}(\beta)$	Jacobi (Legendre) polynomial, trial function used			
	to develop fluid-phase collocation equations			

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P <sub>N</sub> <sup>(1,1/2)</sup> (	z) Jacobi polynomial, trial function used to develop				
	sorbent-phase collocation equations				
q	ligand sorbed-phase concentration, mg/g resin				
a <sup>0</sup>	reference sorbent concentration in Langmuir equilibrium with Co, mg/g resin				
a-	particle-average sorbent concentration, mg/g resin				
ra a	Lancmuir maximum sorbent canacity mg/g resin				
-m O	$a/a_{\rm c}$ unitless sorbent concentration				
~ . 0	$g/g_{a}$ , unitless average sorbent concentration				
~a 0.	Cat z.				
~1 r	sorbent particle radial coordinate cm				
- R	sorbent particle radius cm				
R_	separation factor in Thomas model defined in Table				
L	3				
5	sum-of-squared-errors minimum				
5	colid diffusion Sherwood number for batch corbor				
"h	simulation, defined in equation (4-42)				
<b>a</b> 1	Sherwood number defined in Table 2				
sn1	Sherwood humber derined in Table 2				
<sup>Sh</sup> p	pore diffusion Sherwood number for Datch sorber				
	simulation; defined in equation (4-28)				
t	time, sec				
t'	time following arrival of a fluid particle defined				
	in equation (5-2), sec				
Т	throughput parameter in Thomas model				

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T <sub>ij</sub>	spherical Laplacian discretization matrix for z			
	coordinate			
ប	$C/C_0$ , unitless solution concentration			
ប*	C*/C <sub>0</sub> , unitless interfacial concentration			
u <sub>o</sub>	$C_f/C_0$ at $\beta = 0$			
Ub	$C_b/C_0$ , unitless sorber concentration			
U <sub>f</sub>	$C_{f}/C_{0}$ , unitless bed concentration			
U <sub>fj</sub>	<sup>U</sup> f <sup>at β</sup> j			
Up	C <sub>p</sub> /C <sub>0</sub> , unitless pore concentration			
Upi	<sup>U</sup> p at z <sub>i</sub>			
v	interstitial velocity, cm/sec			
v	batch sorber volume, cm <sup>3</sup>			
V <sub>p</sub>	total volume of sorbent particles, cm <sup>3</sup>			
w <sub>n</sub>	eigenvalue defined by equation (4-23)			
x	fixed-bed axial coordinate, cm			
x <sub>i</sub>	ion-exchange capacity, meq/g resin			
x <sub>1</sub>	ligand-exchange capacity, meq/g resin			
Y	unitless concentration defined in Table 2			
z	ζ <sup>2</sup> , transformed sorbent-radial coordinate			
	(unitless)			
z <sub>m</sub>	electrochemical valence of metal			
z	modified Beer's Law parameter, unitless			
Zz	modified Beer's Law parameter, L soln/mg			
Greek Symbols				
α	equilibrium factor in Langmuir-type isotherm			
β	x/L, unitless axial coordinate			
Y	$\epsilon_p c_0 / (\rho_p q_0)$ , pore-to-sorbed-phase capacity ratio			

<sup>3</sup> b	fixed-bed	void	fraction
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- ε<sub>p</sub> sorbent porosity
- ζ r/R, unitless radial coordinate
- n<sub>h</sub> bed length parameter for solid diffusion model in
  equation (5-61)
- η<sub>1</sub> Liaw bed length parameter defined in equation (5-41)
- np bed length parameter for pore diffusion model in equation (5-55)
- nr Rosen bed length parameter defined in equation
   (5-36)
- $e_h$   $D_h t'/R^2$ , unitless time for fixed-bed simulation using solid diffusion model

 $\theta_1$  Liaw unitless time defined by equation (5-42)

θ<sub>p</sub> D<sub>p</sub>t'/R<sup>2</sup>, unitless time for fixed-bed simulation using pore diffusion model

 $\theta_r$  Rosen unitless time defined by equation (5-38)

k "pseudo-kinetic" coefficient in equations (5-9) and (5-10), cm<sup>4</sup>/(mg·sec)

 $\lambda$  tortuosity of pore diffusion path

§ sorber separation constant defined in equation (4-13)

ξ<sub>1</sub> sorber separation constant defined in Table 2

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\rho_{\rm b} \qquad \rho_{\rm p}(1-\varepsilon_{\rm b}), \text{ bulk-bed sorbent density in H+ form, g}

resin/cm<sup>3</sup>
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 $\rho_{\rm D}$  apparent sorbent density in H+ form, g resin/cm<sup>3</sup>

- $\sigma_0(e, f)$  function defined in equation (5-19)
- $\sigma_1(e, f)$  function defined in equation (5-18)
- $\sigma_2(e,f)$  function defined in equation (5-24)
- $t_c$   $t D_p Y/R^2$ , unitless time for combined-diffusion sorber model
- t D<sub>h</sub>/R<sup>2</sup>, unitless time for solid-diffusion sorber
  model
- \*1 sorber unitless time defined in Table 2
- t D<sub>p</sub>/R<sup>2</sup>, unitless time for pore-diffusion sorber model
- film resistance parameter for fixed-bed simulation
   using solid diffusion model, defined in equation
   (5-62)
- Liaw film resistance parameter defined in equation
   (5-43)
- •<sub>r</sub> Rosen film resistance parameter defined in
  equation (5-37)
- $\rho_p D_g q_0 / (\epsilon_p D_p C_0) = D_g / \gamma D_p$ , surface-to-pore flux ratio

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## APPENDIX A: BATCH SORBER PROGRAMS

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Pore Diffusion with Film Resistance Solid Diffusion with Film Resistance Combined Diffusion with Film Resistance Pore Diffusion without Film Resistance Solid Diffusion without Film Resistance

```
IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*60 TITLE
      CHARACTER*30 XTIT.YTIT
      REAL*8 MASS
      EXTERNAL FA4
      DIMENSION DIF1(15), DIF2(15), DIF3(15), ROOT(15), VEC1(15), VEC2(15),
     \&P(3), STEP(3)
      REAL*4 TMOD1(500), CMOD1(500), TEXP1(60), CEXP1(60), ALFAE1, EPS1, SH1,
     &GAMMA1
      COMMON /SUMTRM/TERM(15,15), AN1(15), GAMMA, BETAP, ALFAE, SH, EPS, NCOL
      COMMON /SERCH/TMOD(500), CMOD(500), OAVG(500), RWORK(260), TEXP(60),
     &CEXP(60), CP(15), D, H, TSTEP, TMIN, IWORK(20), NEO, NWRITE, NEXP, ICOST
      DATA XTIT.YTIT/'
                               UNITLESS TIME
     & UNITLESS SORBER CONCENTRATION '/
С
С
С
       PROGRAMMER: WAYNE BOLDEN
                                     OCTOBER 22, 1985
С
C
      THIS PROGRAM CALCULATES THE LIQUID, DIMENSIONLESS CONCENTRATION
С
      IN A LIGAND BATCH SORBER. IT ASSUMES THAT THE METAL-RESIN HAS
      A POROUS MICROSTRUCTURE. LANGMUIR EQUILIBRIUM EXISTS BETWEEN THE
С
С
      SOLID AND LIQUID PHASES AT EACH POINT IN THE PORE. TRANSPORT IS
С
      GOVERNED BY DIFFUSION OF THE LIGAND IN THE PORE FLUID WHICH
С
      INITIALLY HAS NO LIGAND PRESENT. FILM RESISTANCE AT THE SORBENT
      PARTICLE SURFACE IS IMPORTANT SO A FILM TRANSFER COEFFICIENT
С
С
      MUST BE SUPPLIED AS INPUT DATUM. THE MODEL EQUATIONS (DESCRIBED
С
      IN DETAIL ELSEWHERE) ARE SOLVED NUMERICALLY USING THE METHOD
С
      OF ORTHOGONAL COLLOCATION. AN EFFECTIVE DIFFUSION COEFFICIENT
С
      IS DETERMINED BY PATTERN SEARCH OPTIMIZATION.
                                                    THE RELEVANT
С
      EQUATIONS AND EXPLANATIONS ARE FOUND IN THE FOLLOWING SOURCES:
С
С
      1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL
С
        EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL,
С
        ENGLEWOODS CLIFFS, NJ (1978).
Ç
С
      2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22,
С
         1483 (1967).
С
С
      3) NERETNIEKS, I., 'CHEM. ENG. SCI.,' VOL.31, 107 (1976).
С
С
      4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.32,
С
        619 (1977).
С
¢
      5) RICE, R.G., 'CHEM. ENG. SCI., VOL.37, NO. 1, 83 (1982).
С
Ċ
      6) MOORE, C.F., SMITH, C.L. AND MURRILL, P.W., "MULTIDIMENSIONAL
```

C OPTIMIZATION USING PATERN SEARCH," LOUISIANA STATE UNIVERSITY, С BATON ROUGE (1969). C C----THE NECESSARY INPUT DATA ARE:-----С С - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) TITLE С С С ---SORBENT PROPERTIES---С C - LANGMUIR-TYPE EQUILIBRIUM CONSTANT, UNITLESS ALFAE - REFERENCE SORBENT CONCENTRATION, MG/G RESIN С OREF С BETAP - SORBENT POROSITY, CM\*\*3 PORE/CM\*\*3 PARTICLE Ç - APPARENT SOLID SORBENT DENSITY (IN UNTREATED H+ FORM), RHOP С G/CM\*\*3 PARTICLE С D - DIAMETER OF SORBENT PARTICLES, CM С С ---RUN PARAMETERS---С С TEMP - SYSTEM TEMPERATURE, C Ċ MASS - MASS (IN UNTREATED H+ FORM) OF SORBENT, G С - INITIAL BATCH SORBER CONCENTRATION, MG/CM\*\*3 C0 С v - VOLUME OF BATCH SORBER, CM\*\*3 Н - FILM TRANSFER COEFFICIENT, CM/SEC С С NEXP - NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) C TEXP - SAMPLE TIME, SEC С CEXP - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 С С ---NUMERICAL PARAMETERS---С С ITEST - PARAMETER IDENTIFYING WHETHER OR NOT TO PERFORM PATTERN SEARCH (NO = 0, YES = 1) C . . - PARAMETER DETERMINING WHETHER OR NOT A HARD COPY OF С IPLOT С THE PLOT IS MADE (NO = 0, YES = 1) NCOL - NUMBER OF RADIAL INTERIOR COLLOCATION POINTS C Ċ (MAXIMUM OF 15) С TSTEP - SIZE OF DIMENSIONLESS TIME STEP IN NUMERICAL C INTEGRATION NWRITE - NUMBER OF TIMES THE CALCULATED VALUES ARE WRITTEN С C (MAXIMUM OF 500) С DGUESS - GUESS VALUE OF THE EFFECTIVE DIFFUSIVITY, CM\*\*2/SEC Ċ DSTEP - INCREMENTAL PATTERN SEARCH STEP SIZE, CM\*\*2/SEC С C----THE CALCULATED VALUES ARE:-----С С EPS - SEPARATION FACTOR, UNITLESS С C GAMMA - CAPACITY RATIO (PORE TO SURFACE), UNITLESS С SH - SHERWOOD NUMBER, UNITLESS С С С AN1(J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL

```
С
                 GRADIENT AT PARTICLE SURFACE
С
    TERM(I,J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL
С
С
                LAPLACIAN EVALUATED AT ROOT I
С
C
      CP(I)
             - DIMENSIONLESS SORBENT PORE CONCENTRATION AT
С
                ORTHOGONAL POLYNOMIAL ROOT I
С
С
      CP(NEQ) - DIMENSIONLESS, VOLUME-AVERAGE SORBENT CONCENTRATION
С
С
      CMOD
            - DIMENSIONLESS CONCENTRATION
С
С
С
      READ THE TITLE OF THE SYSTEM TO BE STUDIED.
С
      READ (5,100) TITLE
  100 FORMAT (A60)
С
С
      READ THE SOLID SORBENT PROPERTIES.
С
      READ (5,*) ALFAE, QREF, BETAP, RHOP, D
      ALFAE1 = ALFAE
С
С
С
      READ THE RUN PARAMETERS AND CALCULATE THE SEPARATION
С
     FACTOR.
С
     READ (5,*) TEMP, MASS, CO, V, H, NEXP
     EPS = CO*V/(QREF*MASS)
     EPS1 = EPS
С
С
     READ THE NUMERICAL PARAMETERS; CALCULATE THE CAPACITY RATIO
С
     AND THE GUESS VALUE OF THE SHERWOOD NUMBER.
С
     READ (5,*) ITEST, IPLOT, NCOL, TSTEP, NWRITE, DGUESS, DSTEP
     GAMMA = BETAP*CO/(RHOP*QREF)
     GAMMA1 = GAMMA
     SH = H*D/(2.*DGUESS*BETAP)
С
С
     READ THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
     CONCENTRATIONS.
С
     DO 200 L=1,NEXP
     READ (5,*) TEXP(L), CEXP(L)
     CEXP(L) = CEXP(L)/CO
      CEXP1(L) = CEXP(L)
  200 CONTINUE
C
C
     WRITE THE HEADING AND THE INPUT DATA (AS A CHECK).
С
     WRITE (6,101)
```

```
101 FORMAT(1H1,6X, 'NUMERICAL SIMULATION OF A BATCH SORBER BY'/.
     117X, 'ORTHOGONAL COLLOCATION', /, 18X, 'PORE DIFFUSION MODEL')
      WRITE (6,102) TITLE
  102 FORMAT(///,1X,A60)
      WRITE (6,103)
  103 FORMAT(///, 3X, 'THE INPUT DATA ARE AS FOLLOWS:'//)
      WRITE(6,104) ALFAE
  104 FORMAT(/,' THE LANGMUIR-TYPE EQUILIBRIUM CONSTANT IS ',1PD12.5)
      WRITE(6,105) QREF
  105 FORMAT(/' THE REFERENCE SORBENT CONCENTRATION IS ', 1PD12.5,
     1'MG/G RESIN')
      WRITE (6,106) BETAP
  106 FORMAT(/,' THE SORBENT POROSITY IS ',1PD12.5,' CM**3 PORE/CM**3 P
     1ARTICLE')
      WRITE(6,107) RHOP
  107 FORMAT(/' THE APPARENT SORBENT DENSITY IS ',1PD12.5,' G/CM**3')
      WRITE(6,108) D
  108 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
      WRITE(6,109) TEMP
  109 FORMAT(/' THE TEMPERATURE OF THE SORBER IS ',1PD10.3,' C')
      WRITE(6,110) MASS
  110 FORMAT(/' THE MASS OF SORBENT USED IS ',1PD12.5,' G RESIN')
      WRITE (6,111) CO
  111 FORMAT(/' THE INITIAL BATCH SORBER CONCENTRATION IS ',1PD12.5
     1, ' MG/CM**3')
      WRITE (6,112) V
  112 FORMAT(/' THE BATCH SORBER VOLUME IS ',1PD12.5,' CM**3')
      WRITE (6,113) H
  113 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS ',1PD12.5,' CM/SEC')
      IF (ITEST .EQ. 1) THEN
      WRITE (6,114)
  114 FORMAT(/' A PATTERN SEARCH OPTIMIZATION WILL BE PERFORMED')
      ELSE
      WRITE (6,115)
  115 FORMAT(/' THE SUM OF THE SQUARED ERROR TERM WILL BE CALCULATED',/
     1.' FROM THE GUESS DIFFUSIVITY')
      END IF
      WRITE (6,116) NCOL
  116 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS',
     113)
      WRITE (6,117) TSTEP
  117 FORMAT(/' THE DIMENSIONLESS TIME STEP IS ', 1PD10.3)
      WRITE (6,118) NWRITE
  118 FORMAT(/' THE NUMBER OF OUTPUT CALCULATED VALUES IS', I4)
      WRITE(6,119) DGUESS
  119 FORMAT(/' THE GUESS VALUE OF THE DIFFUSIVITY IS ',1PD12.5,' CM**2
     1/SEC')
      WRITE(6,120) DSTEP
  120 FORMAT(/' THE PATTERN SEARCH STEP SIZE IS ',1PD12.5,' CM**2/SEC')
      BEGIN WRITING THE OUTPUT DATA.
С
С
```

С

```
WRITE (6,121) EPS
  121 FORMAT(//,3X, 'THE CALCULATED VALUES ARE: ',///,' THE SEPARATION FA
     1CTOR IS ',1PD12.5)
      WRITE (6,122) GAMMA
  122 FORMAT(/,' THE CAPACITY RATIO IS ',1PD12.5)
      WRITE(6,123) SH
  123 FORMAT(/' THE GUESS VALUE OF THE SHERWOOD NUMBER IS ',1PD12.5)
      WRITE(6,124)
  124 FORMAT(/,' THE COLLOCATION RADIAL COORDINATES ARE:',/)
      NO = O
      N1 = 1
      NT = NCOL + NO + N1
      ALFA = 1.
      BETA = 0.5
      CALL JCOBI (15, NCOL, NO, N1, ALFA, BETA, DIF1, DIF2, DIF3, ROOT)
      DO 1 I = 1,NT
Ċ
С
      WRITE OUT THE RADIAL COLLOCATION POINTS.
С
      R = DSQRT(ROOT(I))
      WRITE(6,34) I,R
   34 FORMAT(1x, 'R(', 12, ') = ', 1PD12.5)
      CALL DFOPR(15,NCOL,NO,N1,I,1,DIF1,DIF2,DIF3,ROOT,VEC1)
      CALL DFOPR(15,NCOL,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
         DO 2 J = 1.NT
C
С
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
      SPHERICAL LAPLACIAN. NOTE THAT
С
         A(I,J) = VEC1(J)
С
         B(I,J) = VEC2(J)
С
         IF (I .EQ. NT) AN1(J) = VEC1(J)
         TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
         CONTINUE
    2
    1 CONTINUE
С
С
      DEFINE THE NUMBER OF EQUATIONS TO BE INTEGRATED BY LSODE.
С
      NEQ = NT
      IF (ITEST .EQ. 1) THEN
C
С
      PERFORM A PATTERN SEARCH FOR THE OPTIMUM DIFFUSIVITY.
С
      P(1) = DGUESS
      STEP(1) = DSTEP
      CALL PATERN(1, P, STEP, 3, 0, COST)
С
      WRITE THE RESULTS OF THE PATTERN SEARCH.
С
С
      WRITE (6,37) P(1),COST,ICOST,NEXP
   37 FORMAT(///,' THE EFFECTIVE DIFFUSIVITY FOR THIS SORBENT IS',/,
     &5X,1PD12.5, 'CM**2/SEC',/,' THE SUM OF THE SQUARED ERRORS IS '
```

```
&,1PD10.3,' WITH ',12,/,2X,' OF THE ',12,' EXPERIMENTAL DATA POINTS
     & USED IN THE OPTIMIZATION')
      WRITE(6,38) SH
   38 FORMAT(/' THE FINAL VALUE OF THE SHERWOOD NUMBER IS ', 1PD12.5)
      WRITE (6,43) TMIN
   43 FORMAT(' THE MINIMUM INTEGRATION TIME STEP WAS ', 1PD10.3)
С
С
      WRITE OUT THE COLUMN HEADING FOR REMAINING THE OUTPUT VARIABLES.
С
      WRITE (6.39)
   39 FORMAT(///, ' THE MODEL CALCULATIONS GIVE:',//,5X,'TIME',4X,
     &'NUMBER', 5X, 'AVERAGE', 8X, 'BATH', /, 15X, 'OF', 7X, 'SORBENT',
     &4X, 'CONCENTRATION', /, 13X, 'STEPS', 3X, 'CONCENTRATION', /, 2X,
                                      _ ____',/)
     δĽ
      DO 3 I = 1, NWRITE
      TMOD1(I) = TMOD(I)
      CMOD1(I) = CMOD(I)
      WRITE (6,7) TMOD(I), I, QAVG(I), CMOD(I)
    7 FORMAT(1X,1PD10.3,3X,15,2(2X,1PD12.5))
    3 CONTINUE
С
С
      WRITE THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
      TIME VALUES ACCORDING TO THE OPTIMUM DIFFUSIVITY.
С
      WRITE (6,40)
   40 FORMAT(///,' THE EXPERIMENTAL DATA ARE:',//,4X,
     &'TIME',5X,'DIMENSIONLESS',5X,'BATH',/,4X,'(SEC)',8X,'TIME',6X,
                                        _____
     &'CONCENTRATION',/,2X,'__
                               DO 250 L=1.NEXP
      TAUE = 4.*TEXP(L)*P(1)/D**2
      TEXP1(L) = TAUE
      WRITE (6,41) TEXP(L), TAUE, CEXP(L)
   41 FORMAT(1X,1PD10.3,2(2X,1PD12.5))
  250 CONTINUE
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
C
      SAME GRAPH.
С
      THE MODEL CALCULATIONS MAY HAVE BEEN DONE FOR AN EFFECTIVE
C
      DIFFUSIVITY THAT IS DIFFERENT FROM THE OPTIMUM ONE. HOWEVER,
С
      THE PATTERN SEARCH PROCEDURE WILL ALLOW THIS DIFFERENCE TO BE
С
      IN THE LAST DIGIT OF ACCURACY ONLY. THIS CAN BE VERIFIED BY
C
      COMPARING THE OPTIMUM DIFFUSIVITY AND THE DIFFUSIVITY OBTAINED
C
      FROM THE SHERWOOD NUMBER. NONETHELESS, THIS DIFFERENCE SHOULD
С
      BE INCONSEQUENTIAL WITH RESPECT TO THE MODEL-DATA FIT.
C
      SH1 = SH
      IF (IPLOT .EQ. 1) CALL GRAF(NEXP,NWRITE,TEXP1,TMOD1,CEXP1,CMOD1,
     &ALFAE1, GAMMA1, EPS1, SH1, TITLE, XTIT, YTIT)
     ELSE
С
С
      CALCULATE THE SUM OF THE SQUARED ERROR TERM WITH THE GUESS
C
     DIFFUSIVITY.
```

```
C
      WRITE (6,39)
                                                     .
      DO 51 I = 1, NEQ
С
С
      INITIALIZE THE SORBENT CONCENTRATION ARRAY.
С
      CP(I) = 0.
   51 CONTINUE
      TI = 0.0
      TF = TSTEP
      TMIN = TSTEP
С
      PERFORM THE NUMERICAL INTEGRATION FOR NWRITE OUTPUT VALUES
С
С
      THAT ARE IN EQUALLY SPACED INTERVALS OF TSTEP IN THE
C
      DIMENSIONLESS TIME.
С
      DO 53 I = 1, NWRITE
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 260
      LIW = 20
      MF = 10
      CALL LSODE (FA4, NEQ, CP, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
     &RWORK, LRW, IWORK, LIW, JAC, MF)
С
С
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
С
      IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
      IF (ISTATE .LT. 0) GO TO 58
      QAVG(I) = CP(NEQ)
      CMOD(I) = 1. - QAVG(I)/EPS
      TMOD(I) = TF
      WRITE (6,7) TMOD(I), I, QAVG(I), CMOD(I)
С
      TMOD1(I) = TMOD(I)
      TMOD1(I) = TF*D**2/(4.*DGUESS)
      CMOD1(I) = CMOD(I)
      TF = TI + TSTEP
   53 CONTINUE
      GO TO 60
   58 WRITE (6,59) ISTATE, TMOD(I), I, QAVG(I), CMOD(I)
   59 FORMAT(//,6X,'ERROR HALT... ISTATE = ',12,/,6X,'THE LAST COMPUTED
     1 VALUES WERE',/,1X,1PD10.3,3X,15,2(2X,1PD12.5))
      STOP
С
С
      IF NO ERRORS OCCUR IN THE NUMERICAL INTEGRATION, CALCULATE
С
      THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE MODEL
С
      AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
```

```
C
      TSTEP OF EACH OTHER).
С
   60 WRITE (6,40)
      ICOST = 0
      COST = 0.
      NCOM = 1
      DO 61 I = 1,NEXP
      IFLG = 0
      TAUE = 4.*TEXP(I)*DGUESS/D**2
С
      TEXP1(I) = TAUE
      TEXP1(I) = TEXP(I)
      WRITE (6,41) TEXP(I), TAUE, CEXP(I)
         DO 63 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TSTEP) THEN
         COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
С
         COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 62
   63
         CONTINUE
      GO TO 61
   62 \text{ ICOST} = \text{ ICOST} + 1
   61 CONTINUE
      WRITE (6,42) COST, ICOST
   42 FORMAT(///, ' THE SUM OF THE SQUARED ERRORS IS ',1PD10.3,' WITH ',
     &/,2X,12,' OF THE EXPERIMENTAL DATA POINTS USED')
      WRITE (6,43) TMIN
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
Ç
      SAME GRAPH.
С
      SH1 = SH
      IF (IPLOT .EQ. 1) CALL GRAF (NEXP, NWRITE, TEXP1, TMOD1, CEXP1, CMOD1,
     &ALFAE1, GAMMA1, EPS1, SH1, TITLE, XTIT, YTIT)
      END IF
      STOP
      END
С
      SUBROUTINE BOUNDS(P, IOUT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      IOUT = 0
      IF(P(1) .LT. 1.D-08) IOUT = 1
      RETURN
      END
C
      SUBROUTINE PROC(P,COST)
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL FA4
      DIMENSION P(3)
      COMMON /SUMTRM/TERM(15,15),AN1(15),GAMMA,BETAP,ALFAE,SH,EPS,NCOL
```

```
COMMON /SERCH/TMOD(500), CMOD(500), QAVG(500), RWORK(260), TEXP(60),
     &CEXP(60), CP(15), D, H, TSTEP, TMIN, IWORK(20), NEO, NWRITE, NEXP, ICOST
      DO 1 I = 1, NEQ
С
C ·
      INITIALIZE THE SORBENT CONCENTRATION ARRAY.
С
      CP(I) = 0.
    1 CONTINUE
      TI = 0.0
      TF = TSTEP
      TMIN = TSTEP
      SH = H^{D}/(2.*P(1)*BETAP)
      DO 3 I = 1, NWRITE
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 260
      LIW = 20
      MF = 10
      CALL LSODE (FA4, NEQ, CP, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
     &RWORK, LRW, IWORK, LIW, JAC, MF)
С
С
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
С
      IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
      IF (ISTATE .LT. 0) GO TO 8
      QAVG(I) = CP(NEQ)
      CMOD(I) = 1. - QAVG(I)/EPS
      TMOD(I) = TF
      TF = TI + TSTEP
    3 CONTINUE
      GO TO 99
    8 WRITE (6,9) ISTATE, TMOD(I), I, QAVG(I), CMOD(I)
    9 FORMAT(//,6X,'ERROR HALT... ISTATE = ',I2,/,6X,'THE LAST COMPUTED
     1 VALUES WERE',/,1X,1PD10.3,2X,16,2(2X,1PD12.5))
      STOP
Ç
С
      IF NO ERRORS OCCUR IN THE NUMERICAL INTEGRATION, CALCULATE
С
      THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE MODEL
С
      AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
С
      TSTEP OF EACH OTHER).
С
   99 ICOST = 0
      COST = 0.
      NCOM = 1
      DO 101 I = 1, NEXP
      IFLG = 0
      TAUE = 4.*TEXP(I)*P(1)/D**2
```

```
DO 103 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TSTEP) THEN
С
         COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
         COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 102
  103
         CONTINUE
      GO TO 101
  102 \text{ ICOST} = \text{ ICOST} + 1
  101 CONTINUE
      RETURN
      END
С
      SUBROUTINE FA4(NEQ,X,Y,DY)
Ç
С
      THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
С
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H.O-Z)
      DIMENSION Y(NEQ), DY(NEQ)
      COMMON /SUMTRM/TM(15,15), AN1(15), GAMMA, BETAP, ALFAE, SH, EPS, NCOL
      FP(T) = ALFAE^{(1. - (ALFAE - 1.)*T/(1. + (ALFAE - 1.)*T))/
     &(1. + (ALFAE - 1.)*T)
      DENOM(T) = 1. + FP(T)/GAMMA
      U = 1. - Y(NEO)/EPS
Ċ
С
      RECALL, NEQ = NT = NCOL + 1.
С
      SUM2 = 0.
      DO 1 I = 1, NCOL
      TEMPY = Y(I)
      SUM1 = 0.
        DO 2 J = 1,NCOL
        SUM1 = SUM1 + (TM(I,J) - 2.*TM(I,NEQ)*AN1(J)/(2.*AN1(NEQ) +
     &
               SH))*Y(J)
    2
        CONTINUE
      SUM1 = SUM1 + TM(I, NEQ) + SH + U/(2. + AN1(NEQ) + SH)
      DY(I) = SUM1/DENOM(TEMPY)
      SUM2 = SUM2 + AN1(I) + Y(I)
    1 CONTINUE
      DY(NEQ) = 6.*GAMMA*SH*(SUM2 + AN1(NEQ)*U)/(2.*AN1(NEQ) + SH)
      RETURN
      END
```

## Solid Diffusion with Film Resistance

```
IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*60 TITLE
      CHARACTER*30 XTIT, YTIT
      REAL*8 MASS
      EXTERNAL FA2, JA2
      DIMENSION DIF1(15), DIF2(15), DIF3(15), ROOT(15), VEC1(15), VEC2(15),
     &P(3),STEP(3)
      REAL*4 TMOD1(500), CMOD1(500), TEXP1(60), CEXP1(60), ALFAE1, EPS1, SH1
      COMMON /SUMTRM/TERM(15,15), AN1(15), SH, PSI, ALFAE, EPS, NT, NCOL
      COMMON /SERCH/TMOD(500), CMOD(500), QAVG(500), RWORK(422), TEXP(60),
     &CEXP(60),Q(16),D,CO,RHOP,QREF,H,TSTEP,TMIN,IWORK(36),NEQ,NWRITE,
     &NEXP, ICOST
                              UNITLESS TIME
                                                   ١,
      DATA XTIT, YTIT/'
     &'UNITLESS SORBER CONCENTRATION '/
С
С
С
       PROGRAMMER: WAYNE BOLDEN
                                     OCTOBER 22, 1985
C
С
      THIS PROGRAM CALCULATES THE LIQUID, DIMENSIONLESS CONCENTRATION
С
      IN A LIGAND BATCH SORBER. IT ASSUMES THE METAL-RESIN TO BE
С
      A PSEUDO-HOMOGENEOUS SOLID. LANGMUIR EQUILIBRIUM OCCURS AT THE
     LIQUID-SOLID INTERFACE AND IS ACCOMPANIED BY TRANSIENT SPHERICAL
С
     DIFFUSION THROUGH THE INITIALLY FRESH SORBENT PARTICLES.
С
С
     FILM RESISTANCE AT THE SORBENT PARTICLE SURFACE IS IMPORTANT SO
С
     A FILM TRANSFER COEFFICIENT MUST BE SUPPLIED AS INPUT DATUM.
С
     THE MODEL EQUATIONS (DESCRIBED IN DETAIL ELSEWHERE) ARE SOLVED
С
     NUMERICALLY USING THE METHOD OF ORTHOGONAL COLLOCATION. AN
     EFFECTIVE DIFFUSION COEFFICIENT IS DETERMINED BY PATTERN SEARCH
С
С
     OPTIMIZATION. THE RELEVANT EQUATIONS AND EXPLANATIONS ARE FOUND
С
     IN THE FOLLOWING SOURCES:
С
С
     1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL
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        EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL,
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        ENGLEWOODS CLIFFS, NJ (1978).
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     2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22,
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        1483 (1967).
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     3) NERETNIEKS, I., 'CHEM. ENG. SCI.,' VOL.31, 107 (1976).
С
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     4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.32,
С
        619 (1977).
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     5) RICE, R.G., 'CHEM. ENG. SCI.,' VOL.37, NO. 1, 83 (1982).
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     6) MOORE, C.F., SMITH, C.L. AND MURRILL, P.W., "MULTIDIMENSIONAL
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С OPTIMIZATION USING PATERN SEARCH," LOUISIANA STATE UNIVERSITY, С BATON ROUGE (1969). С C----THE NECESSARY INPUT DATA ARE:-----С С TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С С ---SOLID SORBENT PROPERTIES---С С ALFAE - LANGMUIR-TYPE EQUILIBRIUM CONSTANT, UNITLESS С **QREF** - REFERENCE SORBENT CONCENTRATION, MG/G RESIN С RHOP - APPARENT SOLID SORBENT DENSITY (IN UNTREATED H+ FORM), С G/CM\*\*3 PARTICLE С D - DIAMETER OF SORBENT PARTICLES, CM С С ---RUN PARAMETERS---С С TEMP - SYSTEM TEMPERATURE, C С MASS - MASS (IN UNTREATED H+ FORM) OF SORBENT, G С C0 - INITIAL BATCH SORBER CONCENTRATION, MG/CM\*\*3 V - VOLUME OF BATCH SORBER, CM\*\*3 С Ċ н - FILM TRANSFER COEFFICIENT, CM/SEC С NEXP - NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) C TEXP - SAMPLE TIME, SEC CEXP - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 С С С ---NUMERICAL PARAMETERS---С С - PARAMETER IDENTIFYING WHETHER OR NOT TO PERFORM ITEST С PATTERN SEARCH (NO = 0, YES = 1) С IPLOT - PARAMETER DETERMINING WHETHER OR NOT A HARD COPY OF С THE PLOT IS MADE (NO = 0, YES = 1) С PSI - STIFFNESS FACTOR(10\*\*-5 TO 10\*\*-9) - NUMBER OF RADIAL INTERIOR COLLOCATION POINTS С NCOL С (MAXIMUM OF 14) С - SIZE OF DIMENSIONLESS TIME STEP IN NUMERICAL TSTEP С INTEGRATION С NWRITE - NUMBER OF TIMES THE CALCULATED VALUES ARE WRITTEN Ċ (MAXIMUM OF 500) С DGUESS - GUESS VALUE OF THE EFFECTIVE DIFFUSIVITY, CM\*\*2/SEC С DSTEP - INCREMENTAL PATTERN SEARCH STEP SIZE, CM\*\*2/SEC С C----THE CALCULATED VALUES ARE:-----С С EPS SEPARATION FACTOR, UNITLESS С С SH - SHERWOOD NUMBER, UNITLESS С С AN1(J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL С GRADIENT AT PARTICLE SURFACE С

```
С
    TERM(I,J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL
С
                LAPLACIAN EVALUATED AT ROOT I
С
C
              - DIMENSIONLESS SOLID SORBENT CONCENTRATION AT
      Q(I)
С
                ORTHOGONAL POLYNOMIAL ROOT I
С
С
      Q(NEQ) - DIMENSIONLESS, VOLUME-AVERAGE SORBENT CONCENTRATION
С
С
      CMOD
              - DIMENSIONLESS CONCENTRATION
С
С
С
      READ THE TITLE OF THE SYSTEM TO BE STUDIED.
С
      READ (5,100) TITLE
  100 FORMAT (A60)
С
Ċ
      READ THE SOLID SORBENT PROPERTIES; CALCULATE THE EQUILIBRIUM
      FACTOR AND THE REFERENCE SORBENT CONCENTRATION.
С
С
      READ (5,*) ALFAE, QREF, RHOP, D
      ALFAE1 = ALFAE
С
С
     READ THE RUN PARAMETERS AND CALCULATE THE SEPARATION
С
      FACTOR.
С
      READ (5,*) TEMP, MASS, CO, V, H, NEXP
      EPS = CO*V/(OREF*MASS)
      EPS1 = EPS
С
С
      READ THE NUMERICAL PARAMETERS AND CALCULATE THE GUESS VALUE
С
      OF THE SHERWOOD NUMBER.
С
     READ (5,*) ITEST, IPLOT, PSI, NCOL, TSTEP, NWRITE, DGUESS, DSTEP
      SH = H*CO*D/(2.*RHOP*DGUESS*QREF)
С
С
     READ THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
     CONCENTRATIONS.
С
     DO 200 L=1,NEXP
     READ (5,*) TEXP(L), CEXP(L)
      CEXP(L) = CEXP(L)/CO
      CEXP1(L) = CEXP(L)
 200 CONTINUE
С
     WRITE THE HEADING AND THE INPUT DATA (AS A CHECK).
С
С
     WRITE (6,101)
  101 FORMAT(1H1,6X, 'NUMERICAL SIMULATION OF A BATCH SORBER BY'/,
     117X, 'ORTHOGONAL COLLOCATION', /, 18X, 'SOLID DIFFUSION MODEL')
     WRITE (6,102) TITLE
  102 FORMAT(///,1X,A60)
```

```
WRITE (6,103)
103 FORMAT(////,3X,'THE INPUT DATA ARE AS FOLLOWS:'//)
    WRITE(6,104) ALFAE
104 FORMAT(/.' THE LANGMUIR-TYPE EOUILIBRIUM CONSTANT IS ',1PD12.5)
    WRITE(6,105) OREF
105 FORMAT(/' THE REFERENCE SORBENT CONCENTRATION IS ',1PD12.5,
   1'MG/G RESIN')
    WRITE(6,106) RHOP
106 FORMAT(/' THE APPARENT SOLID SORBENT DENSITY IS ',1PD12.5,' G/CM*
   1*3')
    WRITE(6,107) D
107 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
    WRITE(6,108) TEMP
108 FORMAT(/' THE TEMPERATURE OF THE SORBER IS ', 1PD10.3, ' C')
    WRITE(6,109) MASS
109 FORMAT(/' THE MASS OF SORBENT USED IS ',1PD12.5,' G RESIN')
    WRITE (6,110) CO
110 FORMAT(/' THE INITIAL BATCH SORBER CONCENTRATION IS ', 1PD12.5
   1, ' MG/CM**3')
    WRITE (6,111) V
111 FORMAT(/' THE BATCH SORBER VOLUME IS ',1PD12.5,' CM**3')
    WRITE (6,112) H
112 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS ',1PD12.5,' CM/SEC')
    IF (ITEST .EQ. 1) THEN
    WRITE (6,113)
113 FORMAT(/' A PATTERN SEARCH OPTIMIZATION WILL BE PERFORMED')
    ELSE
    WRITE (6,114)
114 FORMAT(/' THE SUM OF THE SOUARED ERROR TERM WILL BE CALCULATED',/
   1,' FROM THE GUESS DIFFUSIVITY')
    END IF
    WRITE (6,115) PSI
115 FORMAT(/' THE STIFFNESS FACTOR IS ',1PD10.3)
    WRITE (6,116) NCOL
116 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS',
   113)
    WRITE (6,117) TSTEP
117 FORMAT(/' THE DIMENSIONLESS TIME STEP IS ',1PD10.3)
    WRITE (6,118) NWRITE
118 FORMAT(/' THE NUMBER OF OUTPUT CALCULATED VALUES IS', I4)
   WRITE(6,119) DGUESS
119 FORMAT(/' THE GUESS VALUE OF THE DIFFUSIVITY IS ',1PD12.5,' CM**2
   1/SEC')
    WRITE(6,120) DSTEP
120 FORMAT(/' THE PATTERN SEARCH STEP SIZE IS ',1PD12.5,' CM**2/SEC')
   BEGIN WRITING THE OUTPUT DATA.
   WRITE(6,121) EPS
121 FORMAT(//,3X, 'THE CALCULATED VALUES ARE:',///,' THE SEPARATION FA
    WRITE(6,122) SH
122 FORMAT(/' THE GUESS VALUE OF THE SHERWOOD NUMBER IS ',1PD12.5)
```

C C

С

```
WRITE(6,123)
  123 FORMAT(/, ' THE COLLOCATION RADIAL COORDINATES ARE: ',/)
      NO = O
      N1 \approx 1
      NT = NCOL + NO + N1
      ALFA = 1.
      BETA = 0.5
      CALL JCOBI (15, NCOL, NO, N1, ALFA, BETA, DIF1, DIF2, DIF3, ROOT)
      DO 1 I = 1,NT
С
С
      WRITE OUT THE RADIAL COLLOCATION POINTS.
С
      R = DSQRT(ROOT(I))
      WRITE(6,34) I,R
   34 FORMAT(1X, 'R(',I2,') = ',1PD12.5)
      CALL DFOPR(15,NCOL,N0,N1,I,1,DIF1,DIF2,DIF3,ROOT,VEC1)
      CALL DFOPR(15,NCOL,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
         DO 2 J = 1, NT
С
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
С
      SPHERICAL LAPLACIAN. NOTE THAT
С
         A(I,J) = VEC1(J)
С
         B(I,J) = VEC2(J)
С
         IF (I .EQ. NT) AN1(J) = VEC1(J)
         TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
         CONTINUE
    2
    1 CONTINUE
С
С
      DEFINE THE NUMBER OF EQUATIONS TO INTEGRATED BY LSODE.
С
      NEQ = NT + 1
      IF (ITEST .EQ. 1) THEN
С
      PERFORM A PATTERN SEARCH FOR THE OPTIMUM DIFFUSIVITY.
С
С
      P(1) = DGUESS
      STEP(1) = DSTEP
      CALL PATERN(1,P,STEP,3,0,COST)
С
С
      WRITE THE RESULTS OF THE PATTERN SEARCH.
С
      WRITE (6,37) P(1),COST,ICOST,NEXP
   37 FORMAT(///,' THE EFFECTIVE DIFFUSIVITY FOR THIS SORBENT IS',/,
     &5X,1PD12.5,' CM**2/SEC',/,' THE SUM OF THE SQUARED ERRORS IS '
     &,1PD10.3,' WITH ',12,/,2X,' OF THE ',12,' EXPERIMENTAL DATA POINTS
     & USED IN THE OPTIMIZATION')
      WRITE(6,38) SH
   38 FORMAT(/' THE FINAL VALUE OF THE SHERWOOD NUMBER IS ',1PD12.5)
      WRITE (6,43) TMIN
   43 FORMAT(' THE MINIMUM INTEGRATION TIME STEP WAS ', 1PD10.3)
С
```

```
С
      WRITE OUT THE COLUMN HEADING FOR REMAINING THE OUTPUT VARIABLES.
С
      WRITE (6,39)
   39 FORMAT(///,'
                     THE MODEL CALCULATIONS GIVE: ',//,5X,'TIME',4X,
     &'NUMBER', 5X, 'AVERAGE', 8X, 'BATH', /, 15X, 'OF', 7X, 'SORBENT',
     &4X, 'CONCENTRATION',/,13X, 'STEPS',3X, 'CONCENTRATION',/,2X,
                                       _ ____'/)
     _'&
      DO 3 I = 1,NWRITE
      TMOD1(I) = TMOD(I)
      CMOD1(I) = CMOD(I)
      WRITE (6,7) TMOD(I), I, QAVG(I), CMOD(I)
    7 FORMAT(1X,1PD10.3,3X,15,2(2X,1PD12.5))
    3 CONTINUE
С
С
      WRITE THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
      TIME VALUES ACCORDING TO THE OPTIMUM DIFFUSIVITY.
С
      WRITE (6,40)
   40 FORMAT(///.'
                     THE EXPERIMENTAL DATA ARE: ', //, 4X,
     &'TIME',5X,'DIMENSIONLESS',5X,'BATH',/,4X,'(SEC)',8X,'TIME',6X,
     &'CONCENTRATION',/,2X,'_
                                         -----
                                ____
                                                                  _',/)
      DO 250 L=1,NEXP
      TAUE = 4.*TEXP(L)*P(1)/D**2
      TEXP1(L) = TAUE
      WRITE (6,41) TEXP(L), TAUE, CEXP(L)
   41 FORMAT(1X, 1PD10.3, 2(2X, 1PD12.5))
  250 CONTINUE
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
С
      THE MODEL CALCULATIONS MAY HAVE BEEN DONE FOR AN EFFECTIVE
С
      DIFFUSIVITY THAT IS DIFFERENT FROM THE OPTIMUM ONE. HOWEVER,
С
      THE PATTERN SEARCH PROCEDURE WILL ALLOW THIS DIFFERENCE TO BE
C
      IN THE LAST DIGIT OF ACCURACY ONLY. THIS CAN BE VERIFIED BY
С
      COMPARING THE OPTIMUM DIFFUSIVITY AND THE DIFFUSIVITY OBTAINED
С
      FROM THE SHERWOOD NUMBER. NONETHELESS, THIS DIFFERENCE SHOULD
С
      BE INCONSEQUENTIAL WITH RESPECT TO THE MODEL-DATA FIT.
C
      SH1 = SH
      IF (IPLOT .EO. 1) CALL GRAF (NEXP, NWRITE, TEXP1, TMOD1, CEXP1, CMOD1,
     &ALFAE1, EPS1, SH1, TITLE, XTIT, YTIT)
      ELSE
С
С
      CALCULATE THE SUM OF THE SQUARED ERROR TERM WITH THE GUESS
С
      DIFFUSIVITY.
C
      WRITE (6,39)
      DO 51 I = 1,NEO
С
С
      INITIALIZE THE SORBENT CONCENTRATION ARRAY.
С
      Q(I) = 0.
```

```
51 CONTINUE
       TI = 0.0
       TF = TSTEP
       TMIN = TSTEP
С
C
       PERFORM THE NUMERICAL INTEGRATION FOR NWRITE OUTPUT VALUES
С
       THAT ARE IN EQUALLY SPACED INTERVALS OF TSTEP IN THE
С
       DIMENSIONLESS TIME.
С
       DO 53 I = 1, NWRITE
       ITOL = 1
       ATOL = 1.D-04
       RTOL = 1.D-04
       ITASK = 1
       ISTATE = 1
       IOPT = 0
       LRW = 422
       LIW = 36
      MF = 21
       CALL LSODE (FA2, NEO, O, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
      &RWORK, LRW, IWORK, LIW, JA2, MF)
C
С
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
С
       IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
       IF (ISTATE .LT. 0) GO TO 58
       QAVG(I) = Q(NEQ)
       CMOD(I) = 1. - QAVG(I)/EPS
       TMOD(I) = TF
       WRITE (6,7) TMOD(I), I, QAVG(I), CMOD(I)
      TMOD1(I) = TMOD(I)
       CMOD1(I) = CMOD(I)
      TF = TI + TSTEP
   53 CONTINUE
       GO TO 60
   58 WRITE (6,59) ISTATE, TMOD(I), I, QAVG(I), CMOD(I)
   59 FORMAT(//,6X,'ERROR HALT... ISTATE = ',I2,/,6X,'THE LAST COMPUTED
      1 VALUES WERE',/,1X,1PD10.3,3X,15,2(2X,1PD12.5))
      STOP
¢
Ċ
      IF NO ERRORS OCCUR IN THE NUMERICAL INTEGRATION, CALCULATE
С
      THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE MODEL
      AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
С
      TSTEP OF EACH OTHER).
C
   60 WRITE (6,40)
      ICOST = 0
      COST = 0.
      NCOM = 1
      DO 61 I = 1, NEXP
      IFLG = 0
```

```
TAUE = 4.*TEXP(I)*DGUESS/D**2
      TEXP1(I) = TAUE
      WRITE (6,41) TEXP(I), TAUE, CEXP(I)
         DO 63 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TSTEP) THEN
         COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
С
         COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 62
   63
         CONTINUE
      GO TO 61
   62 \text{ ICOST} = \text{ ICOST} + 1
   61 CONTINUE
      WRITE (6,42) COST, ICOST
   42 FORMAT(///,' THE SUM OF THE SQUARED ERRORS IS ',1PD10.3,' WITH ',
     &/,2X,12,' OF THE EXPERIMENTAL DATA POINTS USED')
      WRITE (6,43) TMIN
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
С
      SH1 = SH
      IF (IPLOT .EQ. 1) CALL GRAF (NEXP, NWRITE, TEXP1, TMOD1, CEXP1, CMOD1,
     &ALFAE1, EPS1, SH1, TITLE, XTIT, YTIT)
      END IF
      STOP
      END
С
      SUBROUTINE BOUNDS(P, IOUT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      IOUT = 0
      IF(P(1) .LT. 1.D-12) IOUT = 1
      RETURN
      END
С
      SUBROUTINE PROC(P,COST)
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL FA2, JA2
      DIMENSION P(3)
      COMMON /SUMTRM/TERM(15,15), AN1(15), SH, PSI, ALFAE, EPS, NT, NCOL
      COMMON /SERCH/TMOD(500), CMOD(500), OAVG(500), RWORK(382), TEXP(60),
     &CEXP(60),Q(16),D,C0,RHOP,OREF,H,TSTEP,TMIN,IWORK(35),NEO.NWRITE,
     &NEXP, ICOST
      DO 1 I = 1, NEQ
С
С
      INITIALIZE THE SORBENT CONCENTRATION ARRAY.
С
      Q(I) = 0.
    1 CONTINUE
```

```
TI = 0.0
      TF = TSTEP
      TMIN = TSTEP
      SH = H*CO*D/(2.*RHOP*P(1)*QREF)
С
      PERFORM THE NUMERICAL INTEGRATION FOR NWRITE OUTPUT VALUES
      THAT ARE IN EQUALLY SPACED INTERVALS OF TSTEP IN THE
С
      DIMENSIONLESS TIME.
      DO 3 I = 1,NWRITE
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 422
      LIW = 36
      MF = 21
      CALL LSODE (FA2, NEO, O, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
     &RWORK, LRW, IWORK, LIW, JA2, MF)
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
      IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
      IF (ISTATE .LT. 0) GO TO 8
      OAVG(I) = O(NEQ)
      CMOD(I) = 1. - QAVG(I)/EPS
      TMOD(I) = TF
      TF = TI + TSTEP
   3 CONTINUE
      GO TO 99
   & WRITE (6,9) ISTATE,TMOD(I),I,QAVG(I),CMOD(I)
    9 FORMAT(//,6X,'ERROR HALT... ISTATE = ',12,/,6X,'THE LAST COMPUTED
    1 VALUES WERE',/,1X,1PD10.3,3X,15,2(2X,1PD12.5))
      STOP
      IF NO ERRORS OCCUR IN THE NUMERICAL INTEGRATION, CALCULATE
      THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE MODEL
      AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
      TSTEP OF EACH OTHER).
  99 ICOST = 0
      COST = 0.
     NCOM = 1
      DO 101 I = 1,NEXP
      IFLG = 0
      TAUE = 4.*TEXP(1)*P(1)/D**2
        DO 103 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TSTEP) THEN
```

COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))\*\*2

С

С

С

С

С С

С

С С

C

С

С

С

С
```
COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 102
  103
         CONTINUE
      GO TO 101
  102 \text{ ICOST} = \text{ ICOST} + 1
  101 CONTINUE
      RETURN
      END
С
      SUBROUTINE FA2(NEQ,X,Y,DY)
С
С
      THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
С
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(NEQ), DY(NEQ)
      COMMON /SUMTRM/TERM(15,15),AN1(15),SH,PSI,ALFAE,EPS,NT,NCOL
      U = 1. - Y(NEQ)/EPS
      SUM2 = 0.
      DO 1 I = 1,NCOL
      SUM2 = SUM2 + AN1(I)*Y(I)
      SUM1 = 0.
        DO 2 J = 1,NT
        SUM1 = SUM1 + TERM(I,J)*Y(J)
    2
        CONTINUE
      DY(I) = SUM1
    1 CONTINUE
      DY(NT) = (ALFAE*U + 2.*SUM2*((ALFAE - 1.)*Y(NT) - ALFAE)/SH -
     &Y(NT)*(2.*ALFAE*AN1(NT)/SH + 1. + (ALFAE - 1.)*U) +
     &2.*(ALFAE - 1.)*AN1(NT)*Y(NT)**2/SH)/PSI
     DY(NEQ) = 6.*(SUM2 + AN1(NT)*Y(NT))
      RETURN
      END
      SUBROUTINE JA2(NEQ,X,Y,ML,MU,PD,NRPD)
С
С
      THIS SUBROUTINE CALCULATES THE JACOBIAN MATRIX FOR
С
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(NEQ), PD(NRPD, NEQ)
      COMMON /SUMTRM/TERM(15,15), AN1(15), SH, PSI, ALFAE, EPS, NT, NCOL
      U = 1. - Y(NEQ)/EPS
      SUM2 = 0.
      DO 1 I = 1, NCOL
      SUM2 = SUM2 + AN1(I)*Y(I)
        DO 2 J = 1,NT
        PD(I,J) = TERM(I,J)
        CONTINUE
    2
    1 CONTINUE
```

```
DO 3 L = 1,NCOL

PD(NT,L) = 2.*AN1(L)*((ALFAE - 1.)*Y(NT) - ALFAE)/(SH*PSI)

3 CONTINUE

PD(NT,NT) = (2.*((ALFAE - 1.)*SUM2 - ALFAE*AN1(NT))/SH - 1. -

&(ALFAE - 1.)*U + 4.*(ALFAE - 1.)*AN1(NT)*Y(NT)/SH)/PSI

PD(NT,NEQ) = ((ALFAE - 1.)*Y(NT) - ALFAE)/(PSI*EPS)

DO 4 L = 1,NT

PD(NEQ,L) = 6.*AN1(L)

4 CONTINUE

RETURN

END
```

.

Combined Diffusion with Film Resistance

IMPLICIT REAL\*8 (A-H,O-Z) CHARACTER\*60 TITLE CHARACTER\*30 XTIT, YTIT REAL\*8 K, MASS EXTERNAL FA5 DIMENSION DIF1(31), DIF2(31), DIF3(31), ROOT(31), VEC1(31), VEC2(31), &P(3),STEP(3) REAL\*4 TMOD1(60), CMOD1(60), CEXP1(60) COMMON /SUMTRM/TERM(31,31),AN1(31),GAMMA,UPSLN,ALFAE,SH,EPS, &NT.NCOL COMMON /SERCH/TMOD(60), CMOD(60), QAVG(60), RWORK(532), TEXP(60), (20)&NEQ, NEXP C/C0 '/ 1 1 DATA XTIT, YTIT/' TIME, UNITLESS С С С JUNE 25, 1986 PROGRAMMER: WAYNE BOLDEN С С THIS PROGRAM CALCULATES THE LIQUID, DIMENSIONLESS CONCENTRATION С IN A LIGAND BATCH SORBER. IT ASSUMES THAT THE METAL-RESIN HAS Ċ A POROUS MICROSTRUCTURE. LANGMUIR EQUILIBRIUM EXISTS BETWEEN THE С SOLID AND LIQUID PHASES AT EACH POINT IN THE PORE. TRANSPORT IS С GOVERNED BY COMBINED DIFFUSION (PORE DIFFUSION AND SURFACE DIFFUSION) IN THE SORBENT INTERNAL MATRIX (THE PORE FLUID С С INITIALLY HAS NO LIGAND PRESENT). FILM RESISTANCE AT THE SORBENT PARTICLE SURFACE IS IMPORTANT SO A FILM TRANSFER COEFFICIENT C С MUST BE SUPPLIED AS INPUT DATUM. THE MODEL EQUATIONS (DESCRIBED С IN DETAIL ELSEWHERE) ARE SOLVED NUMERICALLY USING THE METHOD C OF ORTHOGONAL COLLOCATION. THE SURFACE DIFFUSION COEFFICIENT С IS DETERMINED BY PATTERN SEARCH OPTIMIZATION. THE RELEVANT EQUATIONS AND EXPLANATIONS ARE FOUND IN THE FOLLOWING SOURCES: С С 1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL С С EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL, С ENGLEWOODS CLIFFS, NJ (1978). С С 2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22, С 1483 (1967). С С 3) NERETNIEKS, I., 'CHEM. ENG. SCI.,' VOL.31, 107 (1976). С 4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.32. C С 619 (1977). С. С 5) RICE, R.G., 'CHEM. ENG. SCI.,' VOL.37, NO. 1, 83 (1982). С

6) MOORE, C.F., SMITH, C.L. AND MURRILL, P.W., "MULTIDIMENSIONAL С С OPTIMIZATION USING PATERN SEARCH," LOUISIANA STATE UNIVERSITY, С BATON ROUGE (1969). С С C TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С С ---SORBENT PROPERTIES---С C - LANGMUIR EQUILIBRIUM CONSTANT, UNITLESS ĸ - SORBENT LIGAND CAPACITY, MG/G RESIN С QM - SORBENT POROSITY, CM\*\*3 PORE/CM\*\*3 PARTICLE С BETAP - APPARENT SOLID SORBENT DENSITY (IN UNTREATED H+ FORM), С RHOP С G/CM\*\*3 PARTICLE . С D - DIAMETER OF SORBENT PARTICLES, CM С С ---RUN PARAMETERS---C С TEMP - SYSTEM TEMPERATURE, C С MASS - MASS (IN UNTREATED H+ FORM) OF SORBENT, G - INITIAL BATCH SORBER CONCENTRATION, MG/CM\*\*3 С C0 - VOLUME OF BATCH SORBER, CM\*\*3 С v H - FILM TRANSFER COEFFICIENT, CM/SEC C - NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) С NEXP С TEXP - SAMPLE TIME, SEC С CEXP - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 С C ---NUMERICAL PARAMETERS---С - PARAMETER IDENTIFYING WHETHER OR NOT TO PERFORM С ITEST PATTERN SEARCH (NO = 0, YES = 1) С - PARAMETER DETERMINING WHETHER OR NOT A HARD COPY OF С IPLOT С THE PLOT IS MADE (NO = 0, YES = 1) - STIFFNESS FACTOR(10\*\*-5 TO 10\*\*-9) С PSI С - NUMBER OF RADIAL INTERIOR COLLOCATION POINTS NCOL С (MAXIMUM OF 30) - THE PORE DIFFUSIVITY, CM\*\*2/SEC С DP - GUESS VALUE OF THE SURFACE DIFFUSIVITY, CM\*\*2/SEC С DSGSS С DSSTP - INCREMENTAL PATTERN SEARCH STEP SIZE FOR SURFACE С DIFFUSIVITY, CM\*\*2/SEC С C-----THE CALCULATED VALUES ARE:------С С QREF - REFERENCE SORBENT CONCENTRATION, MG/G RESIN С С ALFAE - EQUILIBRIUM FACTOR, UNITLESS С С EPS - SEPARATION FACTOR, UNITLESS С С SH - SHERWOOD NUMBER, UNITLESS

```
С
С
      GAMMA - CAPACITY RATIO (PORE TO SURFACE), UNITLESS
С
С
      UPSLN - DIFFUSIVITY RATIO (SURFACE TO PORE), UNITLESS
С
С
     AN1(J)
            - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL
С
                 GRADIENT AT PARTICLE SURFACE
С
С
    TERM(I,J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL
С
                 LAPLACIAN EVALUATED AT ROOT I
С
С
      CP(I)
              - DIMENSIONLESS SORBENT PORE CONCENTRATION AT
С
                 ORTHOGONAL POLYNOMIAL ROOT I
С
      CP(NEQ) - DIMENSIONLESS, VOLUME-AVERAGE SORBENT CONCENTRATION
С
С
С
      U
              - DIMENSIONLESS CONCENTRATION
С
С
С
      READ THE TITLE OF THE SYSTEM TO BE STUDIED.
C
      READ (5,100) TITLE
  100 FORMAT (A60)
С
С
      READ THE SOLID SORBENT PROPERTIES; CALCULATE THE EQUILIBRIUM
С
      FACTOR AND THE REFERENCE SORBENT CONCENTRATION.
С
      READ (5,*) K,QM,BETAP,RHOP,D
      ALFAE = K + 1.
      QREF = K*QM/(1. + K)
Ċ
С
С
      READ THE RUN PARAMETERS AND CALCULATE THE SEPARATION
С
      FACTOR.
С
      READ (5,*) TEMP, MASS, CO, V, H, NEXP
      EPS = CO*V/(QREF*MASS)
С
С
      READ THE NUMERICAL PARAMETERS. CALCULATE THE GUESS VALUE
С
      OF THE SHERWOOD NUMBER, GAMMA AND UPSILON.
.C
      READ (5,*) ITEST, IPLOT, NCOL, DP, DSGSS, DSSTP
      SH = H*D/(2.*DP*BETAP)
      GAMMA = BETAP*CO/(RHOP*OREF)
      UPSLN = RHOP*DSGSS*QREF/(BETAP*DP*C0)
С
C
      READ THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
      CONCENTRATIONS.
С
      DO 200 L=1,NEXP
      READ (5,*) TEXP(L), CEXP(L)
```

```
CEXP(L) = CEXP(L)/CO
      CEXP1(L) = CEXP(L)
  200 CONTINUE
С
      WRITE THE HEADING AND THE INPUT DATA (AS A CHECK).
С
С
     WRITE (6,101)
  101 FORMAT(1H1,6X, 'NUMERICAL SIMULATION OF A BATCH SORBER BY'/,
     117X, 'ORTHOGONAL COLLOCATION', /, 16X, 'COMBINED DIFFUSION MODEL')
     WRITE (6,102) TITLE
  102 FORMAT(///,1X,A60)
     WRITE (6,103)
  103 FORMAT(////,3X,'THE INPUT DATA ARE AS FOLLOWS:'//)
     WRITE(6,104) K
  104 FORMAT(/,' THE LANGMUIR EQUILIBRIUM CONSTANT IS ',1PD12.5)
     WRITE(6,105) QM
  105 FORMAT(/' THE SORBENT LIGAND CAPACITY IS ',1PD12.5,' MG/G RESIN')
     WRITE (6,106) BETAP
  106 FORMAT(/,' THE SORBENT POROSITY IS ',1PD12.5,' CM**3 PORE/CM**3 P
     1ARTICLE')
     WRITE(6,107) RHOP
  107 FORMAT(/' THE APPARENT SORBENT DENSITY IS ',1PD12.5,' G/CM**3')
     WRITE(6,108) D
 108 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
     WRITE(6,109) TEMP
 109 FORMAT(/' THE TEMPERATURE OF THE SORBER IS ',1PD10.3.' C')
     WRITE(6,110) MASS
 110 FORMAT(/' THE MASS OF SORBENT USED IS ', 1PD12.5, ' G RESIN')
     WRITE (6,111) CO
 111 FORMAT(/' THE INITIAL BATCH SORBER CONCENTRATION IS ', 1PD12.5
    1,' MG/CM**3')
     WRITE (6,112) V
 112 FORMAT(/' THE BATCH SORBER VOLUME IS ',1PD12.5,' CM**3')
     WRITE (6,113) H
 113 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS ',1PD12.5,' CM/SEC')
     IF (ITEST .EQ. 1) THEN
     WRITE (6,114)
 114 FORMAT(/' A PATTERN SEARCH OPTIMIZATION WILL BE PERFORMED')
     ELSE
     WRITE (6,115)
 115 FORMAT(/' THE SUM OF THE SQUARED ERROR TERM WILL BE CALCULATED',/
    1,' FROM THE GUESS DIFFUSIVITIES')
     END IF
     WRITE (6,117) NCOL
 117 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS',
    113)
     WRITE(6,118) DP
 118 FORMAT(/' THE VALUE OF THE PORE DIFFUSIVITY IS ',1PD12.5,
    1' CM**2/SEC')
     WRITE(6,119) DSGSS
 119 FORMAT(/' THE GUESS VALUE OF THE SURFACE DIFFUSIVITY IS ',1PD12.5
    1.' CM**2/SEC')
```

```
WRITE(6,120) DSSTP
  120 FORMAT(/' THE SURFACE-DIFFUSIVITY PATTERN SEARCH STEP SIZE IS ',
     &1PD12.5,' CM**2/SEC')
Ċ
С
      BEGIN WRITING THE OUTPUT DATA.
С
      WRITE(6,121) OREF
  121 FORMAT(//,3X,'THE CALCULATED VALUES ARE:',///,' THE REFERENCE SOR
     1BENT CONCENTRATION IS ',1PD12.5,' MG/G RESIN')
      WRITE (6,122) ALFAE
  122 FORMAT(/, ' THE EQUILIBRIUM FACTOR IS ', 1PD12.5)
      WRITE (6,123) EPS
  123 FORMAT(/,' THE SEPARATION FACTOR IS ', 1PD12.5)
      WRITE(6,124) SH
  124 FORMAT(/' THE VALUE OF THE SHERWOOD NUMBER IS ',1PD12.5)
      WRITE(6,125) GAMMA
  125 FORMAT(/' THE CAPACITY RATIO IS ', 1PD12.5)
      WRITE(6,126) UPSLN
  126 FORMAT(/' THE GUESS VALUE OF THE DIFFUSIVITY RATIO IS ',1PD12.5)
      WRITE(6,127)
  127 FORMAT(/, ' THE COLLOCATION RADIAL COORDINATES ARE: ',/)
      NO = O
      N1 = 1
      NT = NCOL + NO + N1
      NEQ = NT + 1
      ALFA = 1.
      BETA = 0.5
      CALL JCOBI (15, NCOL, NO, N1, ALFA, BETA, DIF1, DIF2, DIF3, ROOT)
      DO 1 I = 1,NT
С
C
      WRITE OUT THE RADIAL COLLOCATION POINTS.
С
      R = DSQRT(ROOT(I))
      WRITE(6,34) I,R
   34 FORMAT(1X, 'R(', 12, ') = ', 1PD12.5)
      CALL DFOPR(15,NCOL,NO,N1,I,1,DIF1,DIF2,DIF3,ROOT,VEC1)
      CALL DFOPR(15,NCOL,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
         DO 2 J = 1,NT
С
С
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
Ċ
      SPHERICAL LAPLACIAN. NOTE THAT
С
         A(I,J) = VEC1(J)
С
         B(I,J) = VEC2(J)
C
         IF (I .EQ. NT) AN1(J) = VEC1(J)
         TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
    2
         CONTINUE
    1 CONTINUE
      IF (ITEST .EQ. 1) THEN
С
С
      PERFORM A PATTERN SEARCH FOR THE OPTIMUM DIFFUSIVITY.
С
```

```
P(1) = DSGSS
      STEP(1) = DSSTP
      CALL PATERN(1,P.STEP,2,0,COST)
С
С
      WRITE THE RESULTS OF THE PATTERN SEARCH.
С
      WRITE (6,37) P(1),COST
   37 FORMAT(///,' THE EFFECTIVE DIFFUSIVITY FOR THIS SORBENT IS',/,
     &5X,1PD12.5,' CM**2/SEC',/,' THE SUM OF THE SQUARED ERRORS IS '
     &,1PD10.3)
      WRITE(6,38) UPSLN
   38 FORMAT(/' THE FINAL VALUE OF THE DIFFUSIVITY RATIO IS ', 1PD12.5)
      WRITE (6,44) TMIN
   44 FORMAT(' THE MINIMUM INTEGRATION TIME STEP WAS ', 1PD10.3)
С
Ç
      WRITE OUT THE COLUMN HEADING FOR REMAINING THE OUTPUT VARIABLES.
С
      WRITE (6.40)
   40 FORMAT(///,'
                     THE MODEL CALCULATIONS GIVE: ',//,5X, 'TIME',4X,
     &'NUMBER', 5X, 'AVERAGE', 8X, 'BATH', /, 15X, 'OF', 7X, 'SORBENT',
     &4X, 'CONCENTRATION', /, 13X, 'STEPS', 3X, 'CONCENTRATION', /, 2X,
                           _____
                                                   _'./)
     _'&
      DO 3 I = 1.NEXP
      TMOD1(I) = TMOD(I)
      CMOD1(I) = CMOD(I)
      WRITE (6,7) TMOD(I), I, QAVG(I), CMOD(I)
    7 FORMAT(1X,1PD10.3,3X,15,2(2X,1PD12.5))
    3 CONTINUE
С
С
      WRITE THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
C
      TIME VALUES ACCORDING TO THE OPTIMUM PORE DIFFUSIVITY.
С
      WRITE (6,41)
   41 FORMAT(///,' THE EXPERIMENTAL DATA ARE:',//,4X,
     &'TIME',5X,'DIMENSIONLESS',5X,'BATH',/,4X,'(SEC)',8X,'TIME',6X,
     &'CONCENTRATION',/,2X,'_
                                        _____',/>
      DO 250 L=1,NEXP
      WRITE (6,42) TEXP(L), TMOD1(L), CEXP(L)
   42 FORMAT(1X,1PD10.3,2(2X,1PD12.5))
  250 CONTINUE
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
С
      SAME GRAPH.
¢
      THE MODEL CALCULATIONS MAY HAVE BEEN DONE FOR DIFFUSIVITY
С
      THAT ARE DIFFERENT FROM THE OPTIMUM ONES. HOWEVER,
С
      THE PATTERN SEARCH PROCEDURE WILL ALLOW THIS DIFFERENCE TO BE
С
      IN THE LAST DIGIT OF ACCURACY ONLY. THIS CAN BE VERIFIED BY
С
      COMPARING THE OPTIMUM DIFFUSIVITIES AND THE DIFFUSIVITIES
С
      OBTAINED FROM THE DIFFUSIVITY RATIO. NONETHELESS, THE
С
      DIFFERENCES SHOULD BE INCONSEQUENTIAL WITH RESPECT TO THE
С
      MODEL-DATA FIT.
С
```

```
CALL PLOT(NEXP, TMOD1, CEXP1, CMOD1, TITLE, XTIT, YTIT, IPLOT)
      ELSE
С
С
      CALCULATE THE SUM OF THE SQUARED ERROR TERM WITH THE GUESS
С
      DIFFUSIVITIES.
С
      WRITE (6,40)
      DO 51 I = 1, NEQ
С
С
      INITIALIZE THE SORBENT CONCENTRATION ARRAY.
С
      CP(I) = 0.
   51 CONTINUE
      TI = 0.0
      TF = 4.*TEXP(1)*DP*GAMMA/D**2
      TMIN = TF
      COST = 0.
Ċ
C
      PERFORM THE NUMERICAL INTEGRATION FOR NEQ OUTPUT VALUES
С
      (THE MODEL AND EXPERIMENTAL DIMENSIONLESS TIMES MATCH).
С
      DO 53 I = 1, NEXP
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 532
      LIW = 20
      MF = 10
      CALL LSODE (FA5, NEQ, CP, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
     &RWORK, LRW, IWORK, LIW, JA5, MF)
С
С
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
С
      IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
      IF (ISTATE .LT. 0) GO TO 58
      QAVG(I) = CP(NEQ)
      CMOD(I) = 1. - QAVG(I)/EPS
      TMOD(I) = TF
      WRITE (6,7) TMOD(I), I, QAVG(I), CMOD(I)
      TMOD1(I) = TMOD(I)
      CMOD1(I) = CMOD(I)
      COST = COST + (CEXP(I) - CMOD(I))**2
      IF (I .LT. NEQ) THEN
      TF = 4.*TEXP(I+1)*DP*GAMMA/D**2
      END IF
   53 CONTINUE
      GO TO 60
   58 WRITE (6,59) ISTATE, TMOD(I), I, QAVG(I), CMOD(I)
   59 FORMAT(//,6X,'ERROR HALT... ISTATE = ',I2,/,6X,'THE LAST COMPUTED
```

```
1 VALUES WERE',/,1X,1PD10.3,3X,15,2(2X,1PD12.5))
      STOP
   60 WRITE (6,41)
      DO 61 I = 1,NEXP
      WRITE (6,42) TEXP(I), TMOD1(I), CEXP(I)
   61 CONTINUE
      WRITE (6,43) COST
   43 FORMAT(///, ' THE SUM OF THE SQUARED ERRORS IS ',1PD10.3)
      WRITE (6,44) TMIN
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
С
      CALL PLOT (NEXP, TMOD1, CEXP1, CMOD1, TITLE, XTIT, YTIT, IPLOT)
      END IF
      STOP
      END
С
      SUBROUTINE BOUNDS(P, IOUT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      IOUT = 0
      IF(P(1) .LT. 1.D-15) IOUT = 1
      RETURN
      END
С
      SUBROUTINE PROC(P,COST)
      IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL FA5
      DIMENSION P(3)
      COMMON /SUMTRM/TERM(31,31), AN1(31), GAMMA, UPSLN, ALFAE, SH, EPS,
     &NT, NCOL
      COMMON /SERCH/TMOD(60), CMOD(60), QAVG(60), RWORK(532), TEXP(60),
     &CEXP(60), CP(32), D, H, BETAP, RHOP, QREF, CO, DP, TMIN, IWORK(20),
     &NEQ, NEXP
С
С
      CALCULATE THE SUM OF THE SQUARED ERROR TERM WITH THE GUESS
C
      DIFFUSIVITIES.
С
      DO 51 I = 1, NEQ
С
С
      INITIALIZE THE SORBENT CONCENTRATION ARRAY.
С
      CP(I) = 0.
   51 CONTINUE
      TI = 0.0
      TF = 4.*TEXP(1)*DP*GAMMA/D**2
      TMIN = TF
      UPSLN = RHOP*P(1)*QREF/(BETAP*DP*C0)
      COST = 0.
С
С
      PERFORM THE NUMERICAL INTEGRATION FOR NEQ OUTPUT VALUES
```

```
С
      (THE MODEL AND EXPERIMENTAL DIMENSIONLESS TIMES MATCH).
C
      DO 53 I = 1, NEXP
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 532
      LIW = 20
      MF = 10
      CALL LSODE (FA5, NEQ, CP, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
     &RWORK, LRW, IWORK, LIW, JA5, MF)
С
Ç
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
С
      IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
      IF (ISTATE .LT. 0) GO TO 58
      QAVG(I) = CP(NEQ)
      CMOD(I) = 1. - QAVG(I)/EPS
      TMOD(I) = TF
      COST = COST + (CEXP(I) - CMOD(I))**2
      IF (I .LT. NEQ) THEN
      TF = 4.*TEXP(I+1)*DP*GAMMA/D**2
      END IF
   53 CONTINUE
      GO TO 60
   58 WRITE (6,59) ISTATE, TMOD(I), I, QAVG(I), CMOD(I)
   59 FORMAT(//,6X,'ERROR HALT... ISTATE = ',I2,/,6X,'THE LAST COMPUTED
     1 VALUES WERE',/,1X,1PD10.3,3X,15,2(2X,1PD12.5))
      STOP
   60 RETURN
      END
      SUBROUTINE FA5(NEQ,X,Y,DY)
С
      THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
С
Ç
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(NEQ), DY(NEQ)
      COMMON /SUMTRM/TM(31,31),AN1(31),GAMMA,UPSLN,ALFAE,SH,EPS,
     &NT, NCOL
      G(T) = ALFAE*T/(1. + (ALFAE - 1.)*T)
      GP(T) = ALFAE/(1. + (ALFAE - 1.)*T)**2
      FNC(T) = T + UPSLN*G(T)
      U = 1. - Y(NEQ)/EPS
C
С
      RECALL, NEQ = NT + 1.
С
      SUM2 = 0.
      DO 1 I = 1, NT
```

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```
TMPYI = Y(I)
SUM1 = 0.
D0 2 J = 1,NCOL
TMPYJ = Y(J)
SUM1 = SUM1 + (TM(I,J) - TM(I,NT)*AN1(J)/AN1(NT))*FNC(TMPYJ)
2 CONTINUE
DY(I) = (SUM1 + TM(I,NT)*SH*(U - Y(NT))/(2.*AN1(NT)))/GP(TMPYI)
1 CONTINUE
DY(NEQ) = 3.*SH*(U - Y(NT))
RETURN
END
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Pore Diffusion without Film Resistance

IMPLICIT REAL\*8 (A-H.O-Z) CHARACTER\*60 TITLE CHARACTER\*30 XTIT.YTIT REAL\*8 MASS EXTERNAL FA3 DIMENSION CP(15), DIF1(15), DIF2(15), DIF3(15), ROOT(15), VEC1(15), &VEC2(15), RWORK(260), IWORK(20), P(3), STEP(3) REAL\*4 TMOD1(500), CMOD1(500), TEXP1(60), CEXP1(60), ALFAE1, EPS1, &GAMMA1 COMMON /SUMTRM/TERM(15,15),AN1(15),GAMMA,ALFAE,EPS,NCOL COMMON /SERCH/TMOD(500).CMOD(500).TEXP(60).CEXP(60),NWRITE,NEXP,D, &TSTEP, ICOST DATA XTIT, YTIT/' UNITLESS TIME ١, &'UNITLESS SORBER CONCENTRATION '/ С С С PROGRAMMER: WAYNE BOLDEN OCTOBER 22, 1985 C С THIS PROGRAM CALCULATES THE LIQUID, DIMENSIONLESS CONCENTRATION С IN A LIGAND BATCH SORBER. IT ASSUMES THAT THE METAL-RESIN HAS С A POROUS MICROSTRUCTURE. ALSO, LANGMUIR EOUILIBRIUM EXISTS С BETWEEN THE SOLID AND FLUID PHASES AT EACH POINT IN THE PORE. C TRANSPORT IS GOVERNED BY DIFFUSION OF THE LIGAND IN THE PORE С FLUID WHICH INITIALLY HAS NO LIGAND PRESENT. FILM RESISTANCE С AT THE SORBENT PARTICLE SURFACE IS TAKEN TO BE NEGLIGIBLE SINCE С THE BATH IS RIGOROUSLY AGITATED. THE MODEL EQUATIONS (DESCRIBED С IN DETAIL ELSEWHERE) ARE SOLVED NUMERICALLY USING THE METHOD С OF ORTHOGONAL COLLOCATION. AN EFFECTIVE DIFFUSION COEFFICIENT С IS DETERMINED BY PATTERN SEARCH OPTIMIZATION. THE RELEVANT С EQUATIONS AND EXPLANATIONS ARE FOUND IN THE FOLLOWING SOURCES: С С 1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL С EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL, С ENGLEWOODS CLIFFS, NJ (1978). С С 2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22, С 1483 (1967). С С 3) NERETNIEKS, I., 'CHEM. ENG. SCI.,' VOL.31, 107 (1976). Ç С 4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.32, С 619 (1977). С С 5) RICE, R.G., 'CHEM. ENG. SCI.,' VOL.37, NO. 1, 83 (1982). С С 6) MOORE, C.F., SMITH, C.L. AND MURRILL, P.W., "MULTIDIMENSIONAL

С OPTIMIZATION USING PATERN SEARCH," LOUISIANA STATE UNIVERSITY, С BATON ROUGE (1969). С С С TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С ¢ ---SORBENT PROPERTIES---С ¢ - LANGMUIR-TYPE EQUILIBRIUM CONSTANT, UNITLESS ALFAE С OREF - REFERENCE SORBENT CONCENTRATION, MG/G RESIN С - SORBENT POROSITY, CM\*\*3 PORE/CM\*\*3 PARTICLE BETAP С RHOP - APPARENT SOLID SORBENT DENSITY (IN UNTREATED H+ FORM), С G/CM\*\*3 PARTICLE Ċ D - DIAMETER OF SORBENT PARTICLES, CM C С ---RUN PARAMETERS----С С TEMP - SYSTEM TEMPERATURE, C С MASS - MASS (IN UNTREATED H+ FORM) OF SORBENT, G С C0 - INITIAL BATCH SORBER CONCENTRATION, MG/CM\*\*3 C V - VOLUME OF BATCH SORBER, CM\*\*3 C NEXP - NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) С TEXP - SAMPLE TIME, SEC С CEXP - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 С С ---NUMERICAL PARAMETERS---С C ITEST - PARAMETER IDENTIFYING WHETHER OR NOT TO PERFORM C PATTERN SEARCH (NO = 0, YES = 1) - PARAMETER DETERMINING WHETHER OR NOT A HARD COPY OF С IPLOT С THE PLOT IS MADE (NO = 0, YES = 1) С - NUMBER OF RADIAL INTERIOR COLLOCATION POINTS NCOL Ç (MAXIMUM OF 15) С - SIZE OF DIMENSIONLESS TIME STEP IN NUMERICAL TSTEP ¢ INTEGRATION С NWRITE - NUMBER OF TIMES THE CALCULATED VALUES ARE WRITTEN С (MAXIMUM OF 500) С GUESS VALUE OF THE EFFECTIVE DIFFUSIVITY, CM\*\*2/SEC DGUESS -C DSTEP - INCREMENTAL PATTERN SEARCH STEP SIZE, CM\*\*2/SEC С C----THE CALCULATED VALUES ARE:-----Ç С EPS - SEPARATION FACTOR, UNITLESS С C GAMMA - CAPACITY RATIO (PORE TO SURFACE), UNITLESS С С AN1(J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL С GRADIENT AT PARTICLE SURFACE C TERM(I,J) ~ LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL С

```
С
                LAPLACIAN EVALUATED AT ROOT I
С
С
      CP(I) - DIMENSIONLESS SORBENT PORE CONCENTRATION AT
С
                ORTHOGONAL POLYNOMIAL ROOT I
С
С
      CP(NT) - DIMENSIONLESS, VOLUME-AVERAGE SORBENT CONCENTRATION
C
С
             - DIMENSIONLESS CONCENTRATION
      CMOD
С
С
С
      READ THE TITLE OF THE SYSTEM TO BE STUDIED.
С
      READ (5,100) TITLE
  100 FORMAT (A60)
С
C
      READ THE SOLID SORBENT PROPERTIES.
С
      READ (5,*) ALFAE, QREF, BETAP, RHOP, D
      ALFAE1 = ALFAE
С
С
      READ THE RUN PARAMETERS AND CALCULATE THE SEPARATION
С
      FACTOR.
С
      READ (5,*) TEMP, MASS, CO, V, NEXP
      EPS = CO*V/(OREF*MASS)
      EPS1 = EPS
С
С
      READ THE NUMERICAL PARAMETERS. CALCULATE THE CAPACITY RATIO.
С
      READ (5,*) ITEST, IPLOT, NCOL, TSTEP, NWRITE, DGUESS, DSTEP
      GAMMA = BETAP*CO/(RHOP*QREF)
      GAMMA1 = GAMMA
С
C
     READ THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
      CONCENTRATIONS.
С
     DO 200 L=1,NEXP
     READ (5, *) TEXP(L), CEXP(L)
     CEXP(L) = CEXP(L)/CO
     CEXP1(L) = CEXP(L)
  200 CONTINUE
С
С
     WRITE THE HEADING AND THE INPUT DATA (AS A CHECK).
С
     WRITE (6,101)
  101 FORMAT(1H1,6X, 'NUMERICAL SIMULATION OF A BATCH SORBER BY'/,
     117X, 'ORTHOGONAL COLLOCATION', /, 18X, 'PORE DIFFUSION MODEL')
     WRITE (6,102) TITLE
  102 FORMAT(///,1X,A60)
     WRITE (6,103)
  103 FORMAT(///,3X,'THE INPUT DATA ARE AS FOLLOWS:'//)
```

```
WRITE(6,104) ALFAE
  104 FORMAT(/,' THE LANGMUIR-TYPE EOUILIBRIUM CONSTANT IS ',1PD12.5)
      WRITE(6,105) QREF
  105 FORMAT(/' THE REFERENCE SORBENT CONCENTRATION IS ',1PD12.5,
     1'MG/G RESIN')
      WRITE(6,106) BETAP
  106 FORMAT(/.' THE SORBENT POROSITY IS '.1PD12.5.' CM**3 PORE/CM**3 P
     1ARTICLE')
      WRITE(6,107) RHOP
  107 FORMAT(/' THE APPARENT SORBENT DENSITY IS ',1PD12.5,' G/CM**3 PAR
     1TICLE')
      WRITE(6,108) D
  108 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
      WRITE(6,109) TEMP
  109 FORMAT(/' THE TEMPERATURE OF THE SORBER IS '.1PD10.3.' C')
      WRITE(6,110) MASS
  110 FORMAT(/' THE MASS OF SORBENT USED IS '.1PD12.5.' G RESIN')
      WRITE (6,111) CO
  111 FORMAT(/' THE INITIAL BATCH SORBER CONCENTRATION IS '.1PD12.5
     1, ' MG/CM**3')
     WRITE (6,112) V
  112 FORMAT(/' THE BATCH SORBER VOLUME IS ',1PD12.5,' CM**3')
      IF (ITEST .EQ. 1) THEN
      WRITE (6,113)
  113 FORMAT(/' A PATTERN SEARCH OPTIMIZATION WILL BE PERFORMED')
      ELSE
      WRITE (6,114)
  114 FORMAT(/' THE SUM OF THE SQUARED ERROR TERM WILL BE CALCULATED'./
     1,' FROM THE GUESS DIFFUSIVITY')
      END IF
      WRITE (6.115) NCOL
  115 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS',
     113)
      WRITE (6,116) TSTEP
  116 FORMAT(/' THE DIMENSIONLESS TIME STEP IS ',1PD10.3)
      WRITE (6,117) NWRITE
  117 FORMAT(/' THE NUMBER OF OUTPUT CALCULATED VALUES IS', I4)
      WRITE(6,118) DGUESS
  118 FORMAT(/' THE GUESS VALUE OF THE DIFFUSIVITY IS ',1PD12.5,' CM**2
     1/SEC')
     WRITE(6,119) DSTEP
 119 FORMAT(/' THE PATTERN SEARCH STEP SIZE IS ',1PD12.5,' CM**2/SEC')
      BEGIN WRITING THE OUTPUT DATA.
С
      WRITE(6,120) EPS
 120 FORMAT(//,3X,'THE CALCULATED VALUES ARE:',///,' THE SEPARATION FA
    1CTOR IS ',1PD12.5)
     WRITE (6,121) GAMMA
 121 FORMAT(/,' THE CAPACITY RATIO IS ',1PD12.5)
     WRITE(6,122)
 122 FORMAT(/.' THE COLLOCATION RADIAL COORDINATES ARE:',/)
```

С

С

```
NO = O
      N1 = 1
      NT = NCOL + NO + N1
      ALFA = 1.
      BETA = 0.5
      CALL JCOBI (15, NCOL, NO, N1, ALFA, BETA, DIF1, DIF2, DIF3, ROOT)
      DO 1 I = 1,NT
С
С
      INITIALIZE THE SORBENT PORE CONCENTRATION ARRAY AND WRITE OUT
С
      THE RADIAL COLLOCATION POINTS.
С
      CP(I) = 0.
      R = DSQRT(ROOT(I))
      WRITE(6,34) I,R
   34 FORMAT(1X, 'R(', I2, ') = ', 1PD12.5)
      CALL DFOPR(15, NCOL, NO, N1, I, 1, DIF1, DIF2, DIF3, ROOT, VEC1)
      CALL DFOPR(15,NCOL,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
         DO 2 J = 1,NT
C
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
С
      SPHERICAL LAPLACIAN. NOTE THAT
С
         A(I,J) = VEC1(J)
С
         B(I,J) = VEC2(J)
С
         IF (I .EQ. NT) AN1(J) = VEC1(J)
         TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
         CONTINUE
    2
    1 CONTINUE
C
      WRITE OUT THE COLUMN HEADING FOR THE MODEL CALCULATIONS.
С
С
      WRITE (6,36)
                      THE MODEL CALCULATIONS GIVE: ',//,5X, 'TIME',4X,
   36 FORMAT(///,'
     &'NUMBER', 5X, 'AVERAGE', 8X, 'BATH', /, 15X, 'OF', 7X, 'SORBENT',
   &4X, 'CONCENTRATION',/,13X, 'STEPS',3X, 'CONCENTRATION',/,2X,
                                                ____',/)
     _'&
      TI = 0.0
      TF = TSTEP
      TMIN = TSTEP
      DO 3 I = 1, NWRITE
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 260
      LIW = 20
      MF = 10
      CALL LSODE (FA3, NT, CP, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT, RWORK,
     &LRW, IWORK, LIW, JAC, MF)
```

С

```
DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
 С
 С
       IF (RWORK(11) .LT. TMIN) TMIN = RWORK(11)
       IF (ISTATE .LT. 0) GO TO 8
       U = 1. - CP(NT)/EPS
       TMOD(I) = TF
       CMOD(I) = U
       TMOD1(I) = TF
       CMOD1(I) = U
       WRITE (6,7) TF,I,CP(NT),U
     7 FORMAT(1X,1PD10.3,2X,16,2(2X,1PD12.5))
       TF = TI + TSTEP
     3 CONTINUE
       GO TO 99
     8 WRITE (6,9) ISTATE, TF, I, CP(NT), U
     9 FORMAT(//,6X, 'ERROR HALT... ISTATE = ',12,/,6X, 'THE LAST COMPUTED
      1 VALUES WERE',/,1X,1PD10.3,2X,16,2(2X,1PD12.5))
       STOP
   99 IF (ITEST .EQ. 1) THEN
 С
 С
       PERFORM A PATTERN SEARCH FOR THE OPTIMUM DIFFUSIVITY.
                                                               THE
 С
       ERROR TOLERANCE FOR THE DIFFERENCE BETWEEN THE INDEPENDENT
 С
       VARIABLES (TEXP - TMOD) IS TSTEP. THIS IS NEEDED TO DETERMINE
 С
       THE SUM OF THE SQUARED ERRORS.
 C
       P(1) = DGUESS
       STEP(1) = DSTEP
       CALL PATERN(1,P,STEP,3,0,COST)
 С
 С
       WRITE THE RESULTS OF THE PATTERN SEARCH.
 С
       WRITE (6,37) P(1),COST,ICOST
    37 FORMAT(///,' THE EFFECTIVE DIFFUSIVITY FOR THIS SORBENT IS',/,
      &5X,1PD12.5,' CM**2/SEC',/,' THE SUM OF THE SQUARED ERRORS IS '
      &,1PD10.3,' WITH ',/,2X,12,' OF THE EXPERIMENTAL DATA POINTS USED I
       THE OPTIMIZATION')
       WRITE (6,43) TMIN
    43 FORMAT(' THE MINIMUM INTEGRATION TIME STEP WAS ', 1PD10.3)
С
С
      WRITE THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
. C
       TIME VALUES ACCORDING TO THE OPTIMUM DIFFUSIVITY.
С
      WRITE (6,39)
    39 FORMAT(///,'
                    THE EXPERIMENTAL DATA ARE: ',//,4X,
      &'TIME',5X,'DIMENSIONLESS',5X,'BATH',/,4X,'(SEC)',8X,'TIME',6X,
      &'CONCENTRATION',/,2X,'_
                                                          _____',/)
      DO 250 L=1,NEXP
       TAUE = 4.*TEXP(L)*P(1)/D**2
       TEXP1(L) = TAUE
      WRITE (6,40) TEXP(L), TAUE, CEXP(L)
   40 FORMAT(1X,1PD10.3,2(2X,1PD12.5))
   250 CONTINUE
```

```
С
C
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
C
      IF (IPLOT .EQ. 1) CALL GRAF (NEXP, NWRITE, TEXP1, TMOD1, CEXP1, CMOD1,
     &ALFAE1, GAMMA1, EPS1, TITLE, XTIT, YTIT)
      ELSE
С
С
      CALCULATE THE SUM OF THE SOUARED ERROR TERM WITH THE GUESS
С
      DIFFUSIVITY.
С
      WRITE (6,39)
С
С
      CALCULATE THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE
С
      MODEL AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
С
      TOL=TSTEP OF EACH OTHER).
С
      ICOST = 0
      COST = 0.
      NCOM = 1
      DO 51 I = 1,NEXP
      IFLG = 0
      TAUE = 4.*TEXP(I)*DGUESS/D**2
      TEXP1(I) = TAUE
      WRITE (6,40) TEXP(I), TAUE, CEXP(I)
         DO 53 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TSTEP) THEN
         COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
Ċ
         COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 52
   53
         CONTINUE
      GO TO 51
   52 ICOST = ICOST + 1
   51 CONTINUE
      WRITE (6,42) COST, ICOST
   42 FORMAT(///,' THE SUM OF THE SQUARED ERRORS IS ',1PD10.3,' WITH ',
     &/,2X,12,' OF THE EXPERIMENTAL DATA POINTS USED')
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
C
      IF (IPLOT .EQ. 1) CALL GRAF(NEXP,NWRITE,TEXP1,TMOD1,CEXP1,CMOD1,
     &ALFAE1, GAMMA1, EPS1, TITLE, XTIT, YTIT)
      END IF
      STOP
      END
С
      SUBROUTINE FA3(NEQ,X,Y,DY)
```

```
С
С
      THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
C
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(NEO), DY(NEO)
      COMMON /SUMTRM/TM(15,15),AN1(15),GAMMA,ALFAE,EPS,NCOL
      FP(T) = ALFAE*(1. - (ALFAE - 1.)*T/(1. + (ALFAE - 1.)*T))/
     \&(1. + (ALFAE - 1.)*T)
      DENOM(T) = 1. + FP(T)/GAMMA
      U = 1. - Y(NEQ)/EPS
С
      RECALL, NEQ = NT = NCOL + 1.
С
С
      SUM2 = 0.
      DO 1 I = 1, NCOL
      TEMPY = Y(I)
      SUM1 = 0.
        DO 2 J = 1, NCOL
        SUM1 = SUM1 + TM(I,J)*Y(J)
    2
        CONTINUE
      SUM1 = SUM1 + TM(I, NEQ)*U
      DY(I) = SUM1/DENOM(TEMPY)
      SUM2 = SUM2 + AN1(I)*Y(I)
    1 CONTINUE
      DY(NEQ) = 6.*GAMMA*(SUM2 + AN1(NEQ)*U)
      RETURN
      END
С
      SUBROUTINE BOUNDS (P, IOUT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      IOUT = 0
      IF(P(1) .LT. 1.D-8) IOUT = 1
      RETURN
      END
С
С
      SUBROUTINE PROC(P,COST)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      COMMON /SERCH/TMOD(500), CMOD(500), TEXP(60), CEXP(60), NWRITE, NEXP, D,
     &TOL, ICOST
С
C
      CALCULATE THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE
      MODEL AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
С
      TOL=TSTEP OF EACH OTHER).
С
      ICOST = 0
      COST = 0.
      NCOM = 1
```

```
DO 1 I = 1,NEXP
  IFLG = 0
  TAUE = 4.*TEXP(1)*P(1)/D**2
     DO 3 J = NCOM, NWRITE
     IF (DABS(TAUE - TMOD(J)) .LE. TOL) THEN
     COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
COST = COST + (CEXP(I) - CMOD(J))**2
     NCOM = J + 1
      IFLG = 1
     END IF
     IF (IFLG .EQ. 1) GO TO 2
     CONTINUE
3
  GO TO 1
2 \text{ ICOST} = \text{ ICOST} + 1
1 CONTINUE
  RETURN
  END
```

С

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Solid Diffusion without Film Resistance

IMPLICIT REAL\*8 (A-H,O-Z) CHARACTER\*60 TITLE CHARACTER\*30 XTIT, YTIT REAL\*8 MASS EXTERNAL FA1 DIMENSION Q(15), DIF1(15), DIF2(15), DIF3(15), ROOT(15), VEC1(15), &VEC2(15), RWORK(260), IWORK(20), P(3), STEP(3) REAL\*4 TMOD1(500), CMOD1(500), TEXP1(60), CEXP1(60), ALFAE1, EPS1 COMMON /SUMTRM/TERM(15,15), AN1(15), EPS, ALFAE, NCOL COMMON /SERCH/TMOD(500), CMOD(500), TEXP(60), CEXP(60), NWRITE, NEXP, D, &TSTEP, ICOST DATA XTIT, YTIT/' UNITLESS TIME & UNITLESS SORBER CONCENTRATION '/ С С С PROGRAMMER: WAYNE BOLDEN OCTOBER 22, 1985 С THIS PROGRAM CALCULATES THE LIQUID, DIMENSIONLESS CONCENTRATION C IN A LIGAND BATCH SORBER. IT ASSUMES THE METAL-RESIN TO BE С С A PSEUDO-HOMOGENEOUS SOLID. LANGMUIR EOUILIBRIUM OCCURS AT THE С LIQUID-SOLID INTERFACE AND IS ACCOMPANIED BY TRANSIENT SPHERICAL С DIFFUSION THROUGH THE INITIALLY FRESH SORBENT PARTICLES. С FILM RESISTANCE AT THE SORBENT PARTICLE SURFACE IS TAKEN С TO BE NEGLIGIBLE SINCE THE BATH IS RIGOROUSLY AGITATED. С THE MODEL EQUATIONS (DESCRIBED IN DETAIL ELSEWHERE) ARE SOLVED С NUMERICALLY USING THE METHOD OF ORTHOGONAL COLLOCATION. AN C EFFECTIVE DIFFUSION COEFFICIENT IS DETERMINED BY PATTERN SEARCH С OPTIMIZATION. THE RELEVANT EQUATIONS AND EXPLANATIONS ARE FOUND С IN THE FOLLOWING SOURCES: C 1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL С C EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL, С ENGLEWOODS CLIFFS, NJ (1978). С С 2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22, С 1483 (1967). C С 3) NERETNIEKS, I., 'CHEM. ENG. SCI.,' VOL.31, 107 (1976). С С 4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.32, С 619 (1977). С С 5) RICE, R.G., 'CHEM. ENG. SCI.,' VOL.37, NO. 1, 83 (1982). С С 6) MOORE, C.F., SMITH, C.L. AND MURRILL, P.W., "MULTIDIMENSIONAL OPTIMIZATION USING PATERN SEARCH," LOUISIANA STATE UNIVERSITY, С

С BATON ROUGE (1969). C C----THE NECESSARY INPUT DATA ARE:---------С С TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С С ---SOLID SORBENT PROPERTIES---С С ALFAE - LANGMUIR-TYPE EOUILIBRIUM CONSTANT, UNITLESS С - REFERENCE SORBENT CONCENTRATION, MG/G RESIN OREF С RHOP - APPARENT SOLID SORBENT DENSITY (IN UNTREATED H+ FORM), С G/CM\*\*3 PARTICLE С - DIAMETER OF SORBENT PARTICLES, CM D С С ---RUN PARAMETERS---С Ç TEMP - SYSTEM TEMPERATURE, C Ċ MASS - MASS (IN UNTREATED H+ FORM) OF SORBENT, G С C0 INITIAL BATCH SORBER CONCENTRATION, MG/CM\*\*3 С v - VOLUME OF BATCH SORBER, CM\*\*3 С TEXP - SAMPLE TIME, SEC С NEXP - NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) С - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 CEXP С С ---NUMERICAL PARAMETERS---С С - PARAMETER IDENTIFYING WHETHER OR NOT TO PERFORM ITEST С PATTERN SEARCH (NO = 0, YES = 1) С - PARAMETER DETERMINING WHETHER OR NOT A HARD COPY OF IPLOT С THE PLOT IS MADE (NO = 0, YES = 1) С NUMBER OF RADIAL INTERIOR COLLOCATION POINTS NCOL Ç (MAXIMUM OF 15) С - SIZE OF DIMENSIONLESS TIME STEP IN NUMERICAL TSTEP С INTEGRATION С NWRITE - NUMBER OF TIMES THE CALCULATED VALUES ARE WRITTEN C (MAXIMUM OF 500) С GUESS VALUE OF THE EFFECTIVE DIFFUSIVITY. CM\*\*2/SEC DGUESS -С DSTEP - INCREMENTAL PATTERN SEARCH STEP SIZE, CM\*\*2/SEC С С С EPS - SEPARATION FACTOR, UNITLESS С С AN1(J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL С GRADIENT AT PARTICLE SURFACE С TERM(I,J) - LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL С С LAPLACIAN EVALUATED AT ROOT I С С - DIMENSIONLESS SOLID SORBENT CONCENTRATION AT Q(I) С ORTHOGONAL POLYNOMIAL ROOT I

С С Q(NT)- DIMENSIONLESS, VOLUME-AVERAGE SORBENT CONCENTRATION С С CMOD - DIMENSIONLESS CONCENTRATION С С С READ THE TITLE OF THE SYSTEM TO BE STUDIED. С READ (5,100) TITLE 100 FORMAT (A60) С С READ THE SOLID SORBENT PROPERTIES. С READ (5,\*) ALFAE, OREF, RHOP, D ALFAE1 = ALFAEС С READ THE RUN PARAMETERS AND CALCULATE THE SEPARATION С FACTOR. С READ (5,\*) TEMP, MASS, CO, V, NEXP EPS = C0\*V/(QREF\*MASS)EPS1 = EPSС С READ THE NUMERICAL PARAMETERS. С READ (5,\*) ITEST, IPLOT, NCOL, TSTEP, NWRITE, DGUESS, DSTEP С С READ THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE С CONCENTRATIONS. С DO 200 L=1,NEXP READ (5,\*) TEXP(L), CEXP(L) CEXP(L) = CEXP(L)/COCEXP1(L) = CEXP(L)200 CONTINUE С С WRITE THE HEADING AND THE INPUT DATA (AS A CHECK). С WRITE (6,101) 101 FORMAT(1H1,6X, 'NUMERICAL SIMULATION OF A BATCH SORBER BY'/, 117X, 'ORTHOGONAL COLLOCATION', /, 18X, 'SOLID DIFFUSION MODEL') WRITE (6,102) TITLE 102 FORMAT(///,1X,A60) WRITE (6,103) 103 FORMAT(////,3X,'THE INPUT DATA ARE AS FOLLOWS:'//) WRITE(6,104) ALFAE 104 FORMAT(/,' THE LANGMUIR-TYPE EQUILIBRIUM CONSTANT IS ',1PD12.5) WRITE(6,105) OREF 105 FORMAT(/' THE REFERENCE SORBENT CONCENTRATION IS ',1PD12.5, 1'MG/G RESIN') WRITE(6,106) RHOP

```
106 FORMAT(/' THE APPARENT SOLID SORBENT DENSITY IS '.1PD12.5.' G/CM*
     1*3 PARTICLE')
      WRITE(6,107) D
  107 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
      WRITE(6,108) TEMP
  108 FORMAT(/' THE TEMPERATURE OF THE SORBER IS ',1PD10.3,' C')
      WRITE(6,109) MASS
  109 FORMAT(/' THE MASS OF SORBENT USED IS ',1PD12.5,' G RESIN')
      WRITE (6,110) CO
  110 FORMAT(/' THE INITIAL BATCH SORBER CONCENTRATION IS ',1PD12.5
     1,' MG/CM**3')
      WRITE (6,111) V
  111 FORMAT(/' THE BATCH SORBER VOLUME IS ',1PD12.5,' CM**3')
      IF (ITEST .EQ. 1) THEN
      WRITE (6,112)
  112 FORMAT(/' A PATTERN SEARCH OPTIMIZATION WILL BE PERFORMED')
      ELSE
      WRITE (6,113)
  113 FORMAT(/' THE SUM OF THE SQUARED ERROR TERM WILL BE CALCULATED',/
     1, ' FROM THE GUESS DIFFUSIVITY')
      END IF
      WRITE (6,114) NCOL
  114 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS'.
     113)
      WRITE (6,115) TSTEP
  115 FORMAT(/' THE DIMENSIONLESS TIME STEP IS ',1PD10.3)
      WRITE (6,116) NWRITE
  116 FORMAT(/' THE NUMBER OF OUTPUT CALCULATED VALUES IS', I4)
      WRITE(6,117) DGUESS
  117 FORMAT(/' THE GUESS VALUE OF THE DIFFUSIVITY IS ',1PD12.5,' CM**2
     1/SEC')
      WRITE(6,118) DSTEP
  118 FORMAT(/' THE PATTERN SEARCH STEP SIZE IS ', 1PD12.5, ' CM**2/SEC')
      BEGIN WRITING THE OUTPUT DATA.
С
C
      WRITE(6,119) EPS
  119 FORMAT(//, 3X, 'THE CALCULATED VALUES ARE:',///,' THE SEPARATION FA
     1CTOR IS ',1PD12.5)
      WRITE(6,120)
  120 FORMAT(/, ' THE COLLOCATION RADIAL COORDINATES ARE: ',/)
      NO = O
      N1 = 1
      NT = NCOL + NO + N1
      ALFA = 1.
      BETA = 0.5
      CALL JCOBI (15, NCOL, NO, N1, ALFA, BETA, DIF1, DIF2, DIF3, ROOT)
      DO 1 I = 1.NT
С
С
      INITIALIZE THE SORBENT CONCENTRATION ARRAY AND WRITE OUT THE
С
      RADIAL COLLOCATION POINTS.
С
```

C

```
Q(I) = 0.
      R = DSORT(ROOT(I))
      WRITE(6,34) I,R
   34 FORMAT(1X,'R(',I2,') = ',1PD12.5)
      CALL DFOPR(15,NCOL,N0,N1,I,1,DIF1,DIF2,DIF3,ROOT,VEC1)
      CALL DFOPR(15,NCOL,NO,N1,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
         DO 2 J = 1,NT
С
C
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
      SPHERICAL LAPLACIAN. NOTE THAT
С
         A(I,J) = VEC1(J)
С
         B(I,J) = VEC2(J)
С
         IF (I .EQ. NT) AN1(J) = VEC1(J)
         TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
    2
         CONTINUE
    1 CONTINUE
С
С
      WRITE OUT THE COLUMN HEADING FOR THE MODEL CALCULATIONS.
С
      WRITE (6,36)
   36 FORMAT(///,'
                      THE MODEL CALCULATIONS GIVE: ',//,5X, 'TIME',4X,
     &'NUMBER', 5X, 'AVERAGE', 8X, 'BATH', /, 15X, 'OF', 7X, 'SORBENT',
     &4X, 'CONCENTRATION', /, 13X, 'STEPS', 3X, 'CONCENTRATION', /, 2X,
     &'_
                                              _____',/>
      TI = 0.0
      TF \approx TSTEP
      TMIN = TSTEP
      DO 3 I = 1,NWRITE
      ITOL = 1
      ATOL = 1.D-04
      RTOL = 1.D-04
      ITASK = 1
      ISTATE = 1
      IOPT = 0
      LRW = 260
      LIW = 20
      MF \approx 10
      CALL LSODE (FA1,NT,Q,TI,TF,ITOL,RTOL,ATOL,ITASK,ISTATE,IOPT,RWORK,
     &LRW, IWORK, LIW, JAC, MF)
      DETERMINE THE MINIMUM INTEGRATION STEP SIZE.
      IF (RWORK(11) . LT. TMIN) TMIN = RWORK(11)
      IF (ISTATE .LT. 0) GO TO 8
      U = 1. - Q(NT)/EPS
      TMOD(I) = TF
      CMOD(I) = U
      TMOD1(I) = TF
      CMOD1(I) = U
      WRITE (6,7) TF,I,Q(NT),U
    7 FORMAT(1X,1PD10.3,3X,15,2(2X,1PD12.5))
```

```
С
С
С
```

```
TF = TI + TSTEP
    3 CONTINUE
      GO TO 99
    8 WRITE (6,9) ISTATE, TF, I, Q(NT), U
    9 FORMAT(//,6X, 'ERROR HALT... ISTATE = ',12,/,6X, 'THE LAST COMPUTED
     1 VALUES WERE',/,1X,1PD10.3,3X,15,2(2X,1PD12.5))
      STOP
  99 IF (ITEST .EQ. 1) THEN
С
С
      PERFORM A PATTERN SEARCH FOR THE OPTIMUM DIFFUSIVITY.
С
      P(1) = DGUESS
      STEP(1) = DSTEP
      CALL PATERN(1,P,STEP,3,0,COST)
С
Ċ
      WRITE THE RESULTS OF THE PATTERN SEARCH.
С
      WRITE (6,37) P(1),COST,ICOST
   37 FORMAT(///,'
                    THE EFFECTIVE DIFFUSIVITY FOR THIS SORBENT IS',/,
     &5X,1PD12.5,' CM**2/SEC',/,' THE SUM OF THE SQUARED ERRORS IS '
     &,1PD10.3,' WITH ',/,2X,12,' OF THE EXPERIMENTAL DATA POINTS USED I
      THE OPTIMIZATION')
      WRITE (6,43) TMIN
   43 FORMAT(' THE MINIMUM INTEGRATION TIME STEP WAS ', 1PD10.3)
С
С
      WRITE THE EXPERIMENTAL DATA AND NON-DIMENSIONLIZE THE
С
      TIME VALUES ACCORDING TO THE OPTIMUM DIFFUSIVITY.
С
      WRITE (6,39)
                     THE EXPERIMENTAL DATA ARE: ',//,4X,
   39 FORMAT(///, '
     &'TIME',5X,'DIMENSIONLESS',5X,'BATH',/,4X,'(SEC)',8X,'TIME',6X,
     &'CONCENTRATION',/,2X,'_
                                                                  _'./)
      DO 250 L=1,NEXP
      TAUE = 4.*TEXP(L)*P(1)/D**2
      TEXP1(L) = TAUE
      WRITE (6,40) TEXP(L), TAUE, CEXP(L)
   40 FORMAT(1X,1PD10.3,2(2X,1PD12.5))
  250 CONTINUE
С
C
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
С
      IF (IPLOT .EQ. 1) CALL GRAF(NEXP, NWRITE, TEXP1, TMOD1, CEXP1, CMOD1,
     &ALFAE1, EPS1, TITLE, XTIT, YTIT)
      ELSE
С
С
      CALCULATE THE SUM OF THE SQUARED ERROR TERM WITH THE GUESS
С
      DIFFUSIVITY.
C
      WRITE (6,39)
С
C
      CALCULATE THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE
```

```
С
      MODEL AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
С
      TOL=TSTEP OF EACH OTHER).
С
      ICOST = 0
      COST = 0.
      NCOM = 1
      DO 51 I = 1, NEXP
      IFLG = 0
      TAUE = 4.*TEXP(I)*DGUESS/D**2
      TEXP1(I) = TAUE
      WRITE (6,40) TEXP(I), TAUE, CEXP(I)
         DO 53 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TSTEP) THEN
         COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
С
         COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 52
   53
         CONTINUE
      GO TO 51
   52 ICOST = ICOST + 1
   51 CONTINUE
C
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
С
      IF (IPLOT .EQ. 1) CALL GRAF (NEXP, NWRITE, TEXP1, TMOD1, CEXP1, CMOD1,
     &ALFAE1,EPS1,TITLE,XTIT,YTIT)
      WRITE (6,42) COST, ICOST
   42 FORMAT(///,' THE SUM OF THE SQUARED ERRORS IS ',1PD10.3,' WITH ',
     &/,2X,12,' OF THE EXPERIMENTAL DATA POINTS USED')
      END IF
      STOP
      END
С
      SUBROUTINE FA1(NEQ,X,Y,DY)
С
      THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
С
С
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(NEQ), DY(NEQ)
      COMMON /SUMTRM/TERM(15,15), AN1(15), EPS, ALFAE, NCOL
      U = 1. - Y(NEQ)/EPS
      YNP1 = ALFAE*U/(1. + (ALFAE - 1.)*U)
      SUM2 = 0.
      DO 1 I = 1, NCOL
      SUM1 = 0.
        DO 2 J = 1, NCOL
        SUM1 = SUM1 + TERM(I,J)*Y(J)
```

```
2
       CONTINUE
      DY(I) = SUM1 + TERM(I, NEQ) * YNP1
       SUM2 = SUM2 + AN1(I)*Y(I)
    1 CONTINUE
      DY(NEQ) = 6.*(SUM2 + AN1(NEQ)*YNP1)
      RETURN
      END
С
      SUBROUTINE BOUNDS(P, IOUT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      IOUT = 0
      IF(P(1) .LT. 1.D-12) IOUT = 1
      RETURN
      END
С
      SUBROUTINE PROC(P,COST)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION P(3)
      COMMON /SERCH/TMOD(500), CMOD(500), TEXP(60), CEXP(60), NWRITE, NEXP, D,
     &TOL, ICOST
С
С
      CALCULATE THE SUM OF THE SQUARED ERRORS TERM BY COMPARING THE
С
      MODEL AND EXPERIMENTAL DIMENSIONLESS CONCENTRATIONS THAT OCCUR
С
      AT THEIR CORRESPONDING DIMENSIONLESS TIMES (WHICH ARE WITHIN
С
      TOL=TSTEP OF EACH OTHER).
С
      ICOST = 0
      COST = 0.
      NCOM = 1
      DO 1 I = 1, NEXP
      IFLG = 0
      TAUE = 4.*TEXP(I)*P(1)/D**2
         DO 3 J = NCOM, NWRITE
         IF (DABS(TAUE - TMOD(J)) .LE. TOL) THEN
С
         COST = COST + ((CEXP(I) - CMOD(J))/CEXP(I))**2
         COST = COST + (CEXP(I) - CMOD(J))**2
         NCOM = J + 1
         IFLG = 1
         END IF
         IF (IFLG .EQ. 1) GO TO 2
    3
         CONTINUE
      GO TO 1
    2 \text{ ICOST} = \text{ ICOST} + 1
    1 CONTINUE
      RETURN
      END
```

## APPENDIX B: FIXED-BED PROGRAMS

·

Thomas Model Simulator Thomas Model Design Program Pore-diffusion Model Simulator Solid-diffusion Model Simulator

## Thomas Model Simulator

```
IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER *60 TITLE
      CHARACTER *15 MODNO
      DOUBLE PRECISION LNGTH, N, NT, TVAL(202), T(202), X(202), C(202),
     1MUF,K,KVAL
      REAL*4 NT1(202), VCOL(202), CEXP(202), XEXP(202), XMOD(202), TRU1, R1
      COMMON /PHYPRP/MUF, RHOF, DF
С
С
C
      PROGRAMMER: WAYNE BOLDEN
                                     FEBRUARY 27, 1985
С
С
      THIS PROGRAM CALCULATES THE LIQUID, EFFLUENT-BED, DIMENSIONLESS
С
      CONCENTRATION FOR A LIGAND EXCHANGE COLUMN. IT EMPLOYS THE
С
      THOMAS EQUATION WITH AN AVAILABLE VARIETY OF KINETIC DRIVING
С
      FORCES TO REPRESENT THE NET COMPLEXING RATE OF A PROSPECTIVE
С
      LIGAND. THE KINETIC PARAMETERS ARE ESTIMATED WITH MASS TRANSFER
С
      COEFFICIENTS SINCE ADSORPTION RATES ON POROUS SOLIDS ARE ALMOST
С
      ALWAYS DIFFUSION-CONTROLLED. THIS EFFLUENT CONCENTRATION CAN BE
Ç
      CALCULATED FOR LIGAND SORPTION OR ELUTION RUN CONDITIONS. FOR
С
      COLUMN REGENERATION, IT HAS BEEN ASSUMED THAT THE BED IS
С
      INITIALLY SATURATED (OR VERY NEARLY SO) WITH THE LIGAND OF
С
      INTEREST. THE FLUID PHASE IS ALWAYS ASSUMED TO BE A LIQUID.
С
      THE RELEVANT EQUATIONS AND EXPLANATIONS ARE FOUND IN THE
С
     FOLLOWING SOURCES:
С
C
     1) HIESTER, N.K., AND VERMEULEN, T., 'JOURNAL OF CHEM.
C
        PHYS., ' VOL. 16, NO. 11, 1087, (1948).
С
С
     2) SHERWOOD, T.K., PIGFORD, R.L. AND C.R. WILKE, "MASS
Ç
        TRANSFER," MCGRAW-HILL, NEW YORK (1975), 548.
С
C
     3) TAN, H.K.S., 'CHEM. ENG.,' DEC. 24, 1984, 57.
С
C
     4) HIESTER, N.K., AND VERMEULEN, T., 'CHEM. ENG. PROG.,'
С
        VOL. 48, 1952, 505.
C
С
     5) COSTA, E. DE LUCAS, A. AND M.E. GONZALEZ,
С
         'IND. ENG. CHEM. ENG.', VOL. 23, 1984, 400.
С
С
     6) WILSON, E.J. AND C.J. GEANKOPLIS, 'I & E C FUND.,' VOL.5, NO.1,
С
        9, (1966).
C
C----THE NECESSARY INPUT DATA ARE:-----
С
С
     TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS)
С
```

MUF		SOLUTION PROPER	TIES	
MUF				
MUF				
	-	FLUID VISCOSITY,	CP	
RHOF		FLUID-PHASE DENSI	TY, G/CM**3	
DF	-	FLUID-PHASE DIFFU	SIVITY, CM**2/SE	2C
		SOLID SORBENT P	ROPERTIES	
к	-	ADSORPTION EQUILI	BRIUM CONSTANT,	UNITLESS
Q0	-	SOLID SORBENT LIG	AND CAPACITY, MO	G RESIN
DP	-	EFFECTIVE PARTICL	E-PHASE DIFFUSIV	ITY OF LIGAND,
		CM**2/SEC		
D	-	DIAMETER OF SOLID	PARTICLES, CM	
		FIXED BED PROPE	RTIES	
RHOB	-	BULK DENSITY OF B	ED, G/CM**3	
BETA		FRACTIONAL VOIDAG	E IN BED, CM**3	VOID/CM**3 BED
DB	-	BED DIAMETER, CM		
		RUN PARAMETERS-		•
TEMP	-	COLUMN TEMPERATUR	E, C	maron valanta
CU	-	FEED CONCENTRATIO	N FOR LIGAND SON	PTION, MG/CM**3
2	-	BED LENGTH, CM	ME ONTO /CEO	
QRATE		VOLUMETRIC FLOW R	ATE, UMAAJ/SEC	EODOE EVEDECCION
I	-	F/C O) AS FOLLOWS	KINEIIC DRIVING	FORCE EAFRESSION
		r(c,y) ha rollona		
	TA	I FORWARD I	REVERSE	COMMENT
1		RATE ORDER	RATE ORDER	
i				1
i			<u></u>	Į
i 1		2	2	i -
i				i
j 2		2	1	LANGMUIR
i		i i		KINETICS
3		2 1	0	-
Ι				1
4		1	1	FILM AND PARTICLE
1				DIFFUSION
5		1	0	INDEPENDENT OF
1				• TIME
6		1 1	1	PARTICLE DIFFUSION
		1 1		CONTROLLING
THON .	-	FILM TRANSFER ADJ	JSTMENT FACTOR	
FICA				
ILR	-	NUMBER DESCRIBING	RUN OPTION	
ILR	-	NUMBER DESCRIBING = 1 LIGAND SORP:	RUN OPTION TION (COLUMN LOA	DING)
ILR	-	NUMBER DESCRIBING = 1 LIGAND SORP = -1 LIGAND ELUT	RUN OPTION TION (COLUMN LOA TON (COLUMN REGE	DING) NERATION)
	DF   K   QO   DP   D   RHOB   BETA   DB   TEMP   CO   Z   QRATE   NUMRAT       NUMRAT           NUMRAT           1	DF - K - QO - DP - D - D - RHOB - BETA - DB - TEMP - CO - Z - QRATE - NUMRAT -   NUMRAT -   1 1 2 1 3   4   5   6	DF - FLUID-PHASE DIFFU SOLID SORBENT P K - ADSORPTION EQUILI Q0 - SOLID SORBENT LIG DP - EFFECTIVE PARTICL CM**2/SEC D - DIAMETER OF SOLID FIXED BED PROPE RHOB - BULK DENSITY OF B BETA - FRACTIONAL VOIDAG DB - BED DIAMETER, CM RUN PARAMETERS TEMP - COLUMN TEMPERATURE CO - FEED CONCENTRATION Z - BED LENGTH, CM QRATE - VOLUMETRIC FLOW RE NUMRAT - NUMBER DESCRIBING   F(C,Q) AS FOLLOWS   NUMRAT   FORWARD     RATE ORDER     1 2 2   2 2   3 2   4 1   5 1   6 1   1 2   1 2   1 2   2 2   1 1   2 1   1 1	DF - FLUID-PHASE DIFFUSIVITY, CM**2/SE SOLID SORBENT PROPERTIES K - ADSORPTION EQUILIBRIUM CONSTANT, Q0 - SOLID SORBENT LIGAND CAPACITY, MC DP - EFFECTIVE PARTICLE-PHASE DIFFUSIV CM**2/SEC D - DIAMETER OF SOLID PARTICLES, CM FIXED BED PROPERTIES RHOB - BULK DENSITY OF BED, G/CM**3 BETA - FRACTIONAL VOIDAGE IN BED, CM**3 DB - BED DIAMETER, CM RUN PARAMETERS TEMP - COLUMN TEMPERATURE, C CO - FEED CONCENTRATION FOR LIGAND SOR Z - BED LENGTH, CM QRATE - VOLUMETRIC FLOW RATE, CM**3/SEC NUMRAT - NUMBER DESCRIBING KINETIC DRIVING   C,Q) AS FOLLOWS   NUMRAT   FORWARD   REVERSE   1   2   2   2   2   1   3   2   0   4   1   1   5   1   0   6   1   1

.

C C	VCOL	-	VOLUMETRIC THROUGHPUT, CM**3 (MUST BE GREATER THAN THE BED VOIDAGE VOLUME)		
C C	CEXP	-	EXPERIMENTAL CONCENTRATION, MG/CM**3		
	-THE CAL	CUL	ATED VALUES ARE:		
C					
С	U	-	SUPERFICIAL FLUID VELOCITY, CM/SEC		
С					
С	RESTIM	-	BED RESIDENCE TIME, SEC		
С					
С	Н	-	FLUID-PHASE MASS TRANSFER COEFFICIENT, CM/SEC		
С					
C	KVAL	-	KINETIC PARAMETER, UNITS VARY		
C			CM**3 FLUID/(SEC*MG) FOR NUMRAT = 1 THRU 5		
C			1/SEC FOR NUMRAT = 6		
			NTWENCTANTECC TENAMI AD WINDED OF MEANGERD		
	N	~	DIMENSIONLESS LENGTH OR NUMBER OF TRANSFER		
c c			UNT12		
c c	P	_			
c	Î.		SETAMITON PACION, UNTILLOS		
c	TVAL	-	REAL TIME VALUE. SEC		
C					
С	NT	-	DIMENSIONLESS TIME		
С					
С	Т	-	THROUGHPUT PARAMETER, UNITLESS		
С					
C	X	-	DIMENSIONLESS CONCENTRATION		
C C	*******				
0	*****	***	***************************************		
C C			THE OF THE SUSTEN TO BE STUDIED		
c c	KEND IN		The of the Sistem to be Stopleb.		
C	READ (5	111	) TITLE		
111	FORMAT (A60)				
с					
с	READ THE	s so	DLUTION PROPERTIES.		
с			· · · ·		
	READ (5	,*)	MUF, RHOF, DF		
С					
С	READ THE	E SC	LID SORBENT PROPERTIES.		
С					
-	READ (5,	,*)	K,QO,DP,D		
C					
C 0	READ THE	S F1	XED BED PROPERTIES.		
C	DEND /5	*\			
c	KEND (5)		KNOD, DEIR, DD		
č	READ THE	E RI	N PARAMETERS, CALCULATE THE SUPERFICIAL		
č	VELOCITY	( AN	D THE BED RESIDENCE TIME.		
Ċ					
	READ (5.	*)	TEMP, CO, Z, QRATE, NUMRAT, FTCA, ILR, NTIME		
		•			

```
U = QRATE/(7.853981634D-01*DB**2)
      RESTIM = Z*BETA/U
С
С
     WRITE THE HEADING AND THE INPUT DATA (AS A CHECK).
C
     WRITE (6,10)
   10 FORMAT(1H1,5X,'ANALYSIS OF LIGAND EXCHANGE COLUMN PERFORMANCE BY'/
     121X, 'THE THOMAS MODEL')
     WRITE (6,11) TITLE
  11 FORMAT(///,1X,A60)
     WRITE (6,12)
  12 FORMAT(////, 3X, 'THE INPUT DATA ARE AS FOLLOWS:'//)
     WRITE (6,13) MUF
  13 FORMAT(/' THE FLUID-PHASE VISCOSITY IS ',1PD12.5,' CP')
     WRITE (6.14) RHOF
  14 FORMAT(/' THE FLUID-PHASE DENSITY IS ',1PD12.5,' G/CM**3')
     WRITE (6,15) DF
  15 FORMAT(/' THE FLUID-PHASE DIFFUSIVITY IS ',1PD12.5,' CM**2/SEC')
     WRITE (6,16) K
  16 FORMAT(/' THE ADSORPTION EQUILIBRIUM CONSTANT IS', 1PD12.5)
     WRITE (6.17) 00
  17 FORMAT(/' THE SORBENT LIGAND CAPACITY IS ',1PD12.5,' MG/G RESIN')
     WRITE (6,18) DP
  18 FORMAT(/' THE EFFECTIVE PARTICLE-PHASE DIFFUSIVITY IS ',1PD12.5,
    1' CM**2/SEC')
     WRITE (6,19) D
  19 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS '.1PD12.5.' CM')
     WRITE (6,20) RHOB
  20 FORMAT(/' THE BULK BED DENSITY IS ', 1PD12.5, ' G/CM**3')
     WRITE (6,21) BETA
  21 FORMAT(/' THE FRACTIONAL BED VOIDAGE IS ',1PD12.5,' CM**3 VOID/CM
    1**3 BED')
     WRITE (6,22) DB
  22 FORMAT(/' THE BED DIAMETER IS ',1PD12.5,' CM')
     WRITE (6,23) TEMP
  23 FORMAT(/' THE COLUMN TEMPERATURE IS ',1PD12.5,' C')
     WRITE (6,24) CO
  24 FORMAT(/' THE FEED CONCENTRATION FOR LIGAND SORPTION IS ', 1PD12.5
    1.' MG/CM**3')
     WRITE (6,25) Z
  25 FORMAT(/' THE BED LENGTH IS ', 1PD12.5, ' CM')
     WRITE (6,26) QRATE
  26 FORMAT(/' THE VOLUMETRIC FLOW RATE IS ',1PD12.5,' CM**3/SEC')
     WRITE (6,27) NUMRAT
  27 FORMAT(/' THE KINETIC EXPRESSION DESCRIBING THE NET COMPLEXING',
    1/.' RATE IS REACTION NUMBER', 12)
     WRITE (6,227) FTCA
 227 FORMAT(/' THE FILM TRANSFER ADJUSTMENT FACTOR IS ',1PD9.2)
     IF (ILR .EQ. -1) GO TO 40
     WRITE (6.28)
  28 FORMAT(//'
                   THE COLUMN WAS RUN UNDER LOADING CONDITIONS')
     GO TO 42
```

```
00 10
```

```
40 WRITE (6,29)
   29 FORMAT(//'
                    THE COLUMN WAS RUN UNDER REGENERATION CONDITIONS')
С
С
      THE KINETIC PARAMETER IS CALCULATED BY SUBROUTINE KINET.
С
   42 CALL KINET(D, RHOB, DP, K, CO, U, BETA, QO, NUMRAT, HUN, FTCA, KVAL, IFLG)
      H = FTCA*HUN
      IF (IFLG .EQ. -1) GO TO 35
С
С
      THE DIMENSIONLESS LENGTH IS CALCULATED BY FUNCTION LNGTH.
С
      N = LNGTH(KVAL, RHOB, QO, CO, Z, U, NUMRAT)
      TRU1 = N
С
      THE SEPARATION FACTOR IS CALCULATED BY FUNCTION SEPRTE.
С
С
      R = SEPRTE(K, NUMRAT)
      R1 = R
С
С
      BEGIN WRITING THE OUTPUT DATA. WRITE THE NUMBER OF TRANSFER
      UNITS, THE SEPARATION FACTOR AND THE BED RESIDENCE TIME.
С
С
      WRITE (6,30) HUN
   30 FORMAT(//,3X,'THE CALCULATED VALUES ARE:',
     1///,' THE FILM TRANSFER COEFFICIENT CALCULATED FROM THE',/,
     1' CORRELATION IS ',1PD12.5,' CM/SEC')
      WRITE (6,301) H
  301 FORMAT(/,' THE ACTUAL FILM TRANSFER COEFFICIENT IS ',1PD12.5,
     1' CM/SEC')
      WRITE (6,31) N
   31 FORMAT(/,' THE NUMBER OF TRANSFER UNITS IS ',1PD12.5)
      WRITE (6,32) R
   32 FORMAT(/,' THE SEPARATION FACTOR IS ',1PD12.5)
      WRITE (6,33) RESTIM
   33 FORMAT(/, ' THE BED RESIDENCE TIME IS ', 1PD12.5, ' SEC')
С
С
      WRITE OUT THE COLUMN HEADING FOR THE REMAINING OUTPUT VARIABLES.
С
      WRITE (6,1)
    1 FORMAT(1H1,5X,'TIME',8X,'VOLUMETRIC',4X,'DIMENSIONLESS',
     13X, 'THROUGHPUT',4X, 'DIMENSIONLESS',6X, 'MODEL',6X, 'EXPERIMENTAL'
     2,/,18X,'THROUGHPUT',9X,'TIME',8X,'PARAMETER',4X,'CONCENTRATION',
     32X, 'CONCENTRATION', 2X, 'CONCENTRATION', /, 7X, 'SEC', 11X, 'CM**3',
     354X, 'MG/CM**3', 7X, 'MG/CM**3')
C
С
      INITIALIZE THE SUMMER FOR THE SOUARED ERROR TERM.
С
      SUM = 0.
С
      DO 2 I=1,NTIME
С
С
      AFTER READING THE VOLUMETRIC THROUGHPUT AND THE CORRESPONDING
```

```
С
      EXPERIMENTAL CONCENTRATION, THE REAL TIME AND THE DIMENSIONLESS
С
      TIME ARE CALCULATED. WHEN THE PROCEDURE ENCOUNTERS A TIME VALUE
С
      LESS THAN THE BED RESIDENCE TIME, THE CALCULATIONS CEASE AND AN
С
      ERROR MESSAGE IS PRINTED.
C
      READ (5,*) VCOL(I), CEXP(I)
      TVAL(I) = VCOL(I)/QRATE
      XVEXP = CEXP(I)/CO
      XEXP(I) = XVEXP
      IF (TVAL(I) .LT. RESTIM) GO TO 6
C
С
      THE DIMENSIONLESS TIME IS CALCULATED BY FUNCTION TIME.
С
      NT = TIME(KVAL, CO, TVAL, I, Z, BETA, U, K, NUMRAT)
      NT1(I) = NT
С
С
      THE THROUGHPUT PARAMETER IS CALCULATED.
Ċ
      T(I) = NT/N
      IF (ILR .EQ. -1) GO TO 3
C
С
      THE DIMENSIONLESS CONCENTRATION FOR COLUMN LOADING IS
С
      CALCULATED (AVOIDING NUMERICAL OVERFLOW).
С
      X(I) = DCONCL(N,R,NT,NUMRAT)
      GO TO 4
С
С
      THE DIMENSIONLESS CONCENTRATION FOR COLUMN REGENERATION
С
      IS CALCULATED (AVOIDING NUMERICAL OVERFLOW).
С
    3 X(I) = DCONCR(N,R,NT,NUMRAT)
    4 C(I) = CO*X(I)
С
      CALCULATE THE SQUARED ERROR AND ADD IT TO THE SUM TERM.
С
C
      SUM = SUM + (XVEXP - X(I))**2
C
      XMOD(I) = X(I)
С
С
      FINALLY, ALL DIMENSIONLESS VALUES ARE PRINTED OUT FOR A
С
      GIVEN TIME TVAL.
С
      WRITE (6,5) TVAL(I), VCOL(I), NT, T(I), X(I), C(I), CEXP(I)
    5 FORMAT(/,2X,1PD12.5,3X,1PE12.5,3X,4(1PD12.5,3X),1PE12.5)
    2 CONTINUE
С
      WRITE (6,34) SUM
   34 FORMAT(/,' THE SUM OF THE SQUARED ERRORS IS ',1PD12.5,/,'
                                                                     THE E
     1RROR IS THE DIFFERENCE IN THE MODEL AND EXPERIMENTAL DIMENSIONLESS
     2 CONCENTRATIONS')
С
```

```
MODNO = 'Equation (5-9) '
```
```
IF (NUMRAT .EQ. 2) MODNO = 'Equation (5-10)'
      IF (NUMRAT .EQ. 3) MODNO = 'Thomas Model 3 '
      IF (NUMRAT .EQ. 4) MODNO = 'Thomas Model 4 '
      IF (NUMRAT .EQ. 5) MODNO = 'Thomas Model 5 '
      IF (NUMRAT .EQ. 6) MODNO = 'Thomas Model 6 '
      CALL GRAFIT(NT1, XEXP, XMOD, NTIME, MODNO, ILR, NUMRAT, TITLE, TRU1, R1)
      GO TO 99
    6 WRITE (6,7)
    7 FORMAT(/, ' AT LEAST ONE TIME VALUE WAS LESS THAN THE BED RESIDENC
     1E TIME ')
      GO TO 99
   35 WRITE (6,36)
   36 FORMAT(/,' THE J-FACTOR CORRELATION IS NOT APPROPRIATE; THE FLOWR
     1ATE IS TOO HIGH')
   99 STOP
      END
Ĉ
      SUBROUTINE KINET(D,RHOB,DP,K,CO,U,BETA,QO,NUMRAT,HUN,FTCA,KVAL,
     *IFLG)
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION K, MUF, KP, KI, KVAL
      COMMON /PHYPRP/MUF, RHOF, DF
_____
С
С
        THIS SUBPROGRAM EVALUATES THE KINETIC PARAMETER TO
С
      BE USED IN CALCULATING THE THOMAS-EQUATION DIMENSION-
С
      LESS LENGTH AND TIME.
С
C-----
С
С
      THE PARTICLE SURFACE AREA A IS FIRST CALCULATED.
С
     A = 6.D0*(1.D0 - BETA)/D
С
C
      THE FLUID-PHASE MASS-TRANSFER COEFFICIENT H IS CALCULATED
С
      FROM A J-FACTOR CORRELATION GIVEN IN WILSON ET AL
С
      (PARTICLE REYNOLDS NUMBERS BETWEEN 0.0016 AND 55).
С
      RE = D*U*RHOF/(MUF*1.D-02)
      IF (RE .GT. 55.) GO TO 2
      SC = MUF*1.D-02/(RHOF*DF)
      HUN = 1.09*U/BETA*(RE*SC)**(-2./3.)
      H = FTCA*HUN
С
С
      THE MASS-TRANSFER COEFFICIENT FOR THE SOLID PHASE IS
С
      CALCULATED FROM THE EFFECTIVE DIFFUSIVITY.
С
     KP = 10.D0*DP/(D*(1.D0 - BETA))
С
С
      THE KINETIC PARAMETER IS SET FOR ALL FORWARD FIRST
С
      ORDER KINETIC EXPRESSIONS.
С
```

```
KVAL = H^A/(RHOB^2QO)
      IF (NUMRAT .GE. 4) GO TO 1
С
Ċ
      FOR ALL FORWARD SECOND ORDER EXPRESSIONS, THE CONSTANT-
С
      PATTERN CONDITION (C/C0 = Q/Q0 = 0.5) IS ASSUMED TO
С
      CALCULATE THE KINETIC PARAMETER.
С
      PSI = CO*H/(KP*RHOB)
      PHI = (PSI + Q0)/2.D0
      PARM = K - 1.DO
      IF (NUMRAT .GT. 1) PARM = K
      B = QO*K + PSI - PHI*PARM
      CRATIO = (DSQRT(B**2 + 4.DO*PSI*PHI*PARM) - B)/(2.DO*PSI*PARM)
   KVAL = KVAL*(0.5D0 - CRATIO)/0.25D0
      IF (NUMRAT .EQ. 1) KVAL = KVAL/(1.D0 - 1.D0/K)
      IF (NUMRAT .EQ. 2) KVAL = KVAL/(1.D0 - 2.D0/K)
      GO TO 3
С
С
      THE INTERNAL TRANSFER COEFFICIENT IS CALCULATED ACCORDING TO
С
      THE PROCEDURE OF COSTA ET AL.
С
    1 \text{ KI} = 8.*DP/D
      TCON = (KI + H)/(KI*H)
      KVAL = TCON*A/(RHOB*Q0)
С
С
     IF THE LINEAR KINETICS ARE DIFFUSION-CONTROLLED, THE
     KINETIC PARAMETER IS ASSIGNED ACCORDINGLY.
С
С
      IF (NUMRAT .EQ. 6) KVAL = KP*A
     GO TO 3
    2 \text{ IFLG} = -1
    3 RETURN
     END
С
     FUNCTION LNGTH(KVAL, RHOB, Q0, C0, Z, U, NUMRAT)
     IMPLICIT REAL*8 (A-H,O-Z)
     DOUBLE PRECISION LNGTH, KVAL
C-----
С
С
      THIS SUBPROGRAM CALCULATES THE DIMENSIONLESS LENGTH
С
     FOR THE THOMAS EQUATION AS A FUNCTION OF THE DESIRED
     RATE EXPRESSION (VIA NUMRAT VALUE).
C
С
C--
  C
     LNGTH = RHOB \star KVAL \star QO \star Z/U
     IF(NUMRAT .EQ. 6) LNGTH = LNGTH/CO
     RETURN
     END
C
     FUNCTION SEPRTE(K, NUMRAT)
     IMPLICIT REAL*8 (A-H,O-Z)
```

```
DOUBLE PRECISION K
C-----
                            ____
                                                 ______
С
С
      THIS SUBPROGRAM CALCULATES THE SEPARATION FACTOR
С
     FOR THE THOMAS EQUATION AS A FUNCTION OF THE DESIRED
С
     RATE EXPRESSION (VIA NUMRAT VALUE).
С
        C-----
С
     SEPRTE = 1.D0
     IF (NUMRAT .GE. 4) GO TO 1
     SEPRTE = 0.D0
     IF (NUMRAT .EQ. 1) SEPRTE = 1.DO/K
     IF (NUMRAT .EQ. 2) SEPRTE = 1.DO/(K + 1.DO)
   1 RETURN
     END
С
     FUNCTION TIME (KVAL, CO, TVAL, I, Z, BETA, U, K, NUMRAT)
     IMPLICIT REAL*8 (A-H,O-Z)
     DOUBLE PRECISION K, KVAL, TVAL(1)
_____
С
С
     THIS SUBPROGRAM CALCULATES THE DIMENSIONLESS TIME
C
     FOR THE THOMAS EQUATION AS A FUNCTION OF THE DESIRED
     RATE EXPRESSION (VIA NUMRAT VALUE).
С
С
C-----
С
     TIME = KVAL*(TVAL(I) - Z*BETA/U)
     IF (NUMRAT .GE. 5) GO TO 1
     TIME = TIME * CO
     IF (NUMRAT .EQ. 2) TIME = TIME*(1.D0 + 1.D0/K)
     GO TO 2
   1 IF (NUMRAT .EQ. 5) TIME = 0.D0
   2 RETURN
     END
C
С
     FUNCTION JFUNC(U,V)
     IMPLICIT REAL*8 (A-H,O-Z)
     DOUBLE PRECISION JFUNC
C-
                             _____
С
С
С
    PROGRAMMER: WAYNE BOLDEN MARCH 18, 1985
С
C
      THIS SUBPROGRAM CALCULATES REPRESENTATIVE VALUES OF THE
С
     FUNCTION J(U,V). THE RELEVANT EQUATIONS AND EXPLANATIONS
С
     ARE GIVEN IN THE FOLLOWING SOURCES:
С
С
     1) TAN, H.K.S., 'CHEM. ENG.,' DEC. 24, 1984, 57.
С
```

С 2) HIESTER, N.K., AND VERMEULEN, T., 'CHEM. ENG. PROG.,' С VOL. 48, 1952, 505. С C 3) LIAW, C.H., ET AL., 'AICHE J.,' VOL. 25, NO. 2, 1979, 376. С C 4) SHERWOOD, T.K., ET AL., "MASS TRANSFER," MCGRAW-HILL, С NEW YORK (1975), 567. С \_\_\_\_\_ С С IF THE ARGUMENT U IS LESS THAN OR EQUAL TO 1.D-02, С THE J-FUNCTION VALUE IS SET TO 1.0. IF THE ARGUMENT V С IS LESS THAN OR EQUAL TO 1.D-02, THE J FUNCTION IS SET С TO DEXP(-U). C IF (U .LE. 1.D-02 .OR. V .LE. 1.D-02) GO TO 2 С С IF EITHER OF THE ARGUMENTS IS GREATER THAN 20., THEN THE J-С FUNCTION IS EVALUATED WITH AN ASYMPTOTIC EXPANSION. С IF (U.GT. 20. .OR. V.GT. 20.) GO TO 3 С C IF EITHER ARGUMENT IS A FACTOR OF 20 GREATER THAN THE OTHER, С THEN THE VALUE OF J(U,V) IS OBTAINED FROM THE OBSERVED С BEHAVIOR OF TABULATED VALUES. С IF (U/V .GT. 20.D0 .OR. V/U .GT. 20.D0) GO TO 6 С С OTHERWISE, THE MORE EXACT LOGARITHMIC EXPANSION IS USED. С DUBU = 2.\*UDUBV = 2.\*VD = DMAX1(DUBU, DUBV)N = 20 + IDINT(D)BK = 1.D0SUM2 = 0.D0BIGSUM = 0.D0 DO 1 K = 1, NRK = KSUM1 = SUM2SUM2 = SUM2 + DLOG(RK)ARG1 = (RK - 1.D0)\*DLOG(V) - V - SUM1ARG2 = RK\*DLOG(U) - U - SUM2IF (ARG1 .LT. -174.D0) ARG1 = -174.D0IF (ARG2 .LT. -174.D0) ARG2 = -174.D0IF (ARG1 .GT. 174.D0) ARG1 = 174.D0 IF (ARG2 .GT. 174.D0) ARG2 = 174.D0BK = BK - DEXP(ARG1)BIGSUM = BIGSUM + BK\*DEXP(ARG2) 1 JFUNC = BIGSUM + DEXP(-U)GO TO 7 2 JFUNC = 1.D0

```
IF (V .LE. 1.D-02) JFUNC = DEXP(-U)
      GO TO 7
C
      IF EITHER ARGUMENT IS A FACTOR OF 20 GREATER THAN THE OTHER,
C
Ċ
      THEN THE VALUE OF J(U.V) IS OBTAINED FROM THE OBSERVED
С
      BEHAVIOR OF TABULATED VALUES.
С
    3 IF (U/V .GT. 20.D0 .OR. V/U .GT. 20.D0) GO TO 6
      RTPI = 1.772453851D0
      ARG3 = DSQRT(U) - DSQRT(V)
С
С
      NUMERICAL OVERFLOW CAN OCCUR IN THE APPROXIMATIONS
С
      WHEN DABS(ARG3) IS GREATER THAN 13.2 .
С
      IF (DABS(ARG3) .GT. 13.2D0) GO TO 6
      DENOM = RTPI^{(DSQRT(V) + (U^{V})^{**0.25})}
      TERM2 = DEXP(-ARG3**2)/DENOM
С
С
      IF THE ABSOLUTE VALUE OF ARG3 IS GREATER THAN 7.,
С
      THIS APPROXIMATION IS SIMPLIFIED EVEN FURTHER.
C
      IF (DABS(ARG3) .GT. 7.DO) GO TO 5
      JFUNC = 0.5*(DERFC(ARG3) + TERM2)
      GO TO 7
    5 \text{ JFUNC} = 1. + 0.5 \text{ TERM2}
      IF (ARG3 .GT. 7.) JFUNC = 0.5*(DEXP(-ARG3**2)/(RTPI*ARG3) + TERM2)
      GO TO 7
С
      THESE APPROXIMATIONS WERE MADE BY INSPECTION OF THE TABULATED
С
      VALUES OF J(U,V) AS GIVEN BY SHERWOOD ET AL. (GOOD FOR VERY
С
С
      LARGE VALUES OF U AND V).
С
    6 \text{ JFUNC} = 0.D0
      IF (V/U .GE. 0.95D0 .AND. V/U .LE. 1.1D0) JFUNC = 0.5D0
      IF (V/U .GT. 1.1D0) JFUNC = 1.D0
    7 RETURN
      END
С
      FUNCTION PHIO(U,V)
      IMPLICIT REAL*8 (A-H,O-Z)
------
Ç
С
С
      PROGRAMMER: WAYNE BOLDEN
                                     FEBRUARY 4, 1985
С
С
        THIS SUBPROGRAM CALCULATES REPRESENTATIVE VALUES OF THE J-
С
      FUNCTION INTEGRAND REFERRED TO BY TAN AS THE FUNCTION PHIO.
C
      THE RELEVANT EQUATIONS AND EXPLANATIONS ARE GIVEN IN THE
С
      FOLLOWING SOURCES:
Ċ
Ċ
      1) TAN, H.K.S., 'CHEM. ENG.,' DEC. 24, 1984, 57.
С
```

С 2) SHERWOOD, T.K., ET AL., "MASS TRANSFER," MCGRAW-HILL, С NEW YORK (1975), 567. С С 3) LIAW, C.H., ET AL., 'AICHE J.,' VOL. 25, NO. 2, 1979, 376. С C-----C С IF EITHER U OR V IS LESS THAN OR EQUAL TO 1.D-02, THE ¢ PHIO FUNCTION VALUE IS SET TO DEXP(-(U+V)). С IF (U .LE. 1.D-02 .OR. V .LE. 1.D-02) GO TO 2 С С IF EITHER OF THE ARGUMENTS IS GREATER THAN 10., AN С APPROXIMATION OF THE PHIO FUNCTION IS USED. С IF (U .GT. 10.D0 .OR. V .GT. 10.D0) GO TO 3 С С IF EITHER ARGUMENT IS A FACTOR OF 20 GREATER THAN THE OTHER. С THEN THE VALUE OF SMALLER ARGUMENT IS TAKEN TO BE ZERO. C IF (U/V .GT. 20.D0 .OR. V/U .GT. 20.D0) GO TO 2 С С OTHERWISE, THE MORE EXACT LOGARITHMIC EXPANSION IS USED. С DUBU = 2.\*UDUBV = 2.\*VD = DMAX1(DUBU, DUBV)N = 20 + IDINT(D)BK = 1.D0SUM2 = 0.D0BIGSUM = 0.D0DO 1 K = 1, NRK = KSUM1 = SUM2SUM2 = SUM2 + DLOG(RK)ARG1 = (RK - 1.D0)\*DLOG(V) - V - SUM1ARG2 = RK\*DLOG(U) - U - SUM2IF (ARG1 .LT. -174.D0) ARG1 = -174.D0IF (ARG2 .LT. -174.D0) ARG2 = -174.D0 IF (ARG1 .GT. 174.D0) ARG1 = 174.D0 IF (ARG2 .GT. 174.D0) ARG2 = 174.D0 BK = BK - DEXP(ARG1)BIGSUM = BIGSUM + BK\*(RK/U - 1.)\*DEXP(ARG2)1 PHIO = DEXP(-U) - BIGSUMGO TO 4 2 ARG = U + VIF (ARG .GT. 174.D0) GO TO 31 PHIO = DEXP(-ARG)GO TO 4 С С IF EITHER ARGUMENT IS A FACTOR OF 20 GREATER THAN THE OTHER, С THEN THE VALUE OF SMALLER ARGUMENT IS TAKEN TO BE ZERO.

```
С
    3 IF (U/V .GT. 20.D0 .OR. V/U .GT. 20.D0) GO TO 2
      ARG3 = DSQRT(U) - DSQRT(V)
С
С
      NUMERICAL OVERFLOW CAN OCCUR IN THE APPROXIMATIONS
С
      WHEN DABS(ARG3) IS GREATER THAN 13.2 .
C
      IF (DABS(ARG3) .GT. 13.2D0) GO TO 31
      RTPI2 = 3.544907702D0
      DENOM = DSQRT(V) + (U*V)**0.25
      FACTOR = 1.D0 + ARG3/DENOM + (V/U)**0.25/(8.D0*DENOM**2)
      PHIO = DEXP(-ARG3**2)*FACTOR/(DSQRT(U)*RTPI2)
      GO TO 4
   31 \text{ PHIO} = 0.00
    4 RETURN
      END
C 'C
С
      FUNCTION DCONCL(N,R,NT,NUMRAT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION JFUNC, N, NT
С
C-----
              ------
С
C
       THIS SUBPROGRAM CALCULATES THE DIMENSIONLESS CONCENTRATION
C
      FOR COLUMN LOADING CONDITIONS AS A FUNCTION OF THE DESIRED
С
      RATE EXPRESSION (VIA NUMRAT VALUE).
С
С
      RTPI = 1.772453851D0
      RTPI2 = 3.544907702D0
      IF (NUMRAT .GE. 3) GO TO 2
      IF (NT .GT. 10.D0 .OR. N .GT. 10.D0) GO TO 3
С
С
      THE APPROPRIATE CALCULATIONS ARE MADE FOR SMALL ARGUMENT
С
      VALUES USING REACTION RATE EXPRESSION 1 OR 2.
С
      ARGLOG = JFUNC(R*N,NT)
      FACTOR = JFUNC(R*NT,N)
      PHI1 = FACTOR*(1.D0 - PHI0(R*NT,N)/FACTOR)
      G = DLOG(PHI1) - DLOG(ARGLOG) + (R - 1.D0)*(NT - N)
      GO TO 5
    2 IF (NUMRAT .EQ. 4 .OR. NUMRAT .EQ. 6) GO TO 4
С
С
      THE CALCULATIONS ARE MADE FOR REACTION RATE EXPRESSION
C
      3 OR 5.
С
      IF (N .GT. 174.D0) GO TO 20
      ARGLOG = 1.DO - DEXP(-N)
      G = N + DLOG(ARGLOG)
      IF (NUMRAT .EQ. 3) G = G - NT
```

```
GO TO 5
   20 G = N
       IF (NUMRAT .EQ. 3) G = G - NT
       GO TO 5
C
С
       CALCULATIONS ARE MADE FOR LARGE ARGUMENT VALUES
С
      USING REACTION RATE EXPRESSION 1 OR 2.
С
    3 \text{ ARGN} = \text{DSQRT}(R*NT) - \text{DSQRT}(N)
      ARGD = DSQRT(R*N) - DSQRT(NT)
      IF (ARGN .LT. -13.2D0 .OR. ARGD .LT. -13.2D0) GO TO 35
      IF (DABS(ARGN) .LT. 7.D0) GO TO 32
      VALN = 1.DO/ARGN
      IF (ARGN .LT. -7.DO) VALN = RTP12*DEXP(ARGN**2)
      IF (DABS(ARGD) .LT. 7.DO) GO TO 33
   31 \text{ VALD} = 1.00/\text{ARGD}
      IF (ARGD .LT. -7.D0) VALD = RTP12*DEXP(ARGD**2)
      GO TO 34
   32 VALN = RTPI*(DERFC(ARGN))*DEXP(ARGN**2)
      IF (DABS(ARGD) .GT. 7.D0) GO TO 31
   33 VALD = RTPI*(DERFC(ARGD))*DEXP(ARGD**2)
   34 \text{ ADTRM} = (R*N*NT)**0.25
      XINV = 1.D0 + (VALN - 1.D0/(DSQRT(R*NT) + ADTRM))/(VALD + 1.D0/
     1(DSQRT(NT) + ADTRM))
      DCONCL = 1.D0/XINV
      GO TO 99
   35 IF (ARGN .LT. -7.DO .AND. ARGD .LT. -7.DO) GO TO 36
      DCONCL = 0.D0
      IF (ARGN .GT. 0.D0) DCONCL = 1.D0
      GO TO 99
   36 G = (R - 1.D0)*(NT - N)
      GO TO 5
С
С
      THIS IS WHERE CALCULATIONS ARE MADE FOR REACTION RATE
С
      EXPRESSION 4 OR 6.
Ċ
    4 DCONCL = JFUNC(N,NT)
      GO TO 99
С
С
    5 IF (G .GT. 174.D0 .OR. G .LT. -174.D0) GO TO 50
      XINV = 1.DO + DEXP(G)
      DCONCL = 1.DO/XINV
      GO TO 99
   50 DCONCL = 0.D0
      IF (G .LT. -174.D0) DCONCL = 1.D0
   99 RETURN
      END
С
      FUNCTION DCONCR(N,R,NT,NUMRAT)
      IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION JFUNC, N, NT
```

С -----C---С C THIS SUBPROGRAM CALCULATES THE DIMENSIONLESS CONCENTRATION С FOR COLUMN LOADING CONDITIONS AS A FUNCTION OF THE DESIRED С RATE EXPRESSION (VIA NUMRAT VALUE). C C-----С IF (NUMRAT .GE. 3) GO TO 2 IF (NT .GT. 10.D0 .OR. N .GT. 10.D0) GO TO 3 С С THE APPROPRIATE CALCULATIONS ARE MADE FOR SMALL ARGUMENT С VALUES USING REACTION RATE EXPRESSION 1 OR 2. С FACTOR = JFUNC(NT, R\*N) $PHI1 = FACTOR^{+}(1.D0 - PHI0(NT, R^{+}N)/FACTOR)$ ARGLOG = JFUNC(N, R\*NT)G = (R - 1.D0)\*(NT - N) + DLOG(ARGLOG) - DLOG(PHI1)GO TO 5 2 IF (NUMRAT .EQ. 4 .OR. NUMRAT .EQ. 6) GO TO 4 С С THE CALCULATIONS ARE MADE FOR REACTION RATE EXPRESSION С 3 OR 5. С IF (NUMRAT .EQ. 3) GO TO 29 IF (R\*N .GT. 174.D0) GO TO 20 ARGLOG = 1.DO - DEXP(-R\*N)G = -R\*N - DLOG(ARGLOG)GO TO 5 20 G = -R\*NGO TO 5 29 DCONCR = N/NTGO TO 99 С С THIS IS WHERE CALCULATIONS ARE MADE FOR LARGE ARGUMENT С VALUES USING REACTION RATE EXPRESSION 1 OR 2. С 3 RTPI = 1.772453851D0RTPI2 = 3.544907702D0ARGN = DSQRT(N) - DSQRT(R\*NT)ARGD = DSQRT(NT) - DSQRT(R\*N)IF (ARGN .LT. -13.2D0 .OR. ARGD .LT. -13.2D0) GO TO 35 IF (DABS(ARGN) .LT. 7.DO) GO TO 32 VALN = 1.DO/ARGNIF (ARGN .LT. -7.D0) VALN = RTP12\*DEXP(ARGN\*\*2) IF (DABS(ARGD) .LT. 7.DO) GO TO 33 31 VALD = 1.DO/ARGDIF (ARGD .LT. -7.D0) VALD = RTP12\*DEXP(ARGD\*\*2) GO TO 34 32 VALN = RTPI\*(DERFC(ARGN))\*DEXP(ARGN\*\*2) IF (DABS(ARGD) .GT. 7.D0) GO TO 31

```
33 VALD = RTPI*(DERFC(ARGD))*DEXP(ARGD**2)
   34 \text{ ADTRM} = (R*N*NT)**0.25
      DENOM = VALD - 1.DO/(DSQRT(NT) + ADTRM)
      IF (DENOM .LE. 1.D-60) DENOM = VALD
      XINV = 1.D0 + (VALN + 1.D0/(DSQRT(R*NT) + (R*N*NT)**0.25))/DENOM
      DCONCR = 1.DO/XINV
      GO TO 99
   35 IF (ARGN .LT. -7.DO .AND. ARGD .LT. -7.DO) GO TO 36
      DCONCR = 0.D0
      IF (ARGN .GT. 0.D0) DCONCR = 1.D0
      GO TO 99
   36 G = (R - 1.D0)*(NT - N)
      GO TO 5
С
С
      THIS IS WHERE CALCULATIONS ARE MADE FOR REACTION RATE
С
      EXPRESSION 4 OR 6.
С
    4 FACTOR = JFUNC(NT,N)
      IF (FACTOR .LE. 1.D-60) GO TO 41
      PHI1 = FACTOR*(1.D0 - PHI0(NT,N)/FACTOR)
      DCONCR = PHI1
      GO TO 99
   41 DCONCR = 0.D0
      GO TO 99
    5 IF (G .GT. 174.D0 .OR. G .LT. -174.D0) GO TO 50
      XINV = 1.D0 + DEXP(G)
      DCONCR = 1.DO/XINV
      GO TO 99
   50 DCONCR = 0.D0
      IF (G .LT. -174.D0) DCONCR = 1.D0
   99 RETURN
      END
```

```
IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER *60 TITLE
      DOUBLE PRECISION JFUNC, LNGTH, N, NT, MUF, K, KVAL
      COMMON /PHYPRP/MUF, RHOF, DF
      COMMON /PARAM1/K, KVAL, CO, QO, RHOB, TERM2, TERM3
      COMMON /PARAM2/DNTDZ, DNTDT, NUMRAT, ILT, Z, TVAL, N, NT, R, BETA, U
С
С
С
       PROGRAMMER: WAYNE BOLDEN
                                      APRIL 8, 1985
С
Ċ
      THIS PROGRAM DESIGNS AN APPROPRIATE BED LENGTH OR BREAKTHROUGH
С
      TIME FOR A LIGAND EXCHANGE COLUMN.
                                         IT EMPLOYS THE THOMAS
С
      EQUATION WITH AN AVAILABLE VARIETY OF KINETIC DRIVING
С
      FORCES TO REPRESENT THE NET COMPLEXING RATE OF A PROSPECTIVE
С
      LIGAND. THE KINETIC PARAMETERS ARE ESTIMATED WITH MASS TRANSFER
С
      COEFFICIENTS SINCE ADSORPTION RATES ON POROUS SOLIDS ARE ALMOST
С
      ALWAYS DIFFUSION-CONTROLLED. THE DESIGN BED LENGTH OR BREAK-
С
      THROUGH TIME IS DETERMINED BY NEWTON-RHAPSON ITERATION FOR
С
      COLUMN LOADING CONDITIONS. THE FLUID PHASE IS ALWAYS ASSUMED TO
      BE A LIQUID. THE RELEVANT EQUATIONS AND EXPLANATIONS ARE FOUND
С
С
      IN THE FOLLOWING SOURCES:
Ċ
C
      1) HIESTER, N.K., AND VERMEULEN, T., 'JOURNAL OF CHEM.
С
         PHYS., ' VOL. 16, NO. 11, 1087, (1948).
С
С
      2) SHERWOOD, T.K., PIGFORD, R.L. AND C.R. WILKE, "MASS
С
         TRANSFER," MCGRAW-HILL, NEW YORK (1975), 548.
C
С
      3) TAN, H.K.S., 'CHEM. ENG.,' DEC. 24, 1984, 57.
С
C
      4) HIESTER, N.K., AND VERMEULEN, T., 'CHEM. ENG. PROG.,'
С
         VOL. 48, 1952, 505.
С
С
      5) COSTA, E. DE LUCAS, A. AND M.E. GONZALEZ,
С
         'IND. ENG. CHEM. ENG.', VOL. 23, 1984, 400.
С
С
      6) WILSON, E.J. AND C.J. GEANKOPLIS, 'I & E C FUND.,' VOL.5, NO.1,
Ċ
         9, (1966).
С
С
      THE NEWTON-RHAPSON PROCEDURE IS DONE 20 TIMES BEFORE A
С
      A WEGSTEIN ACCELERATION STEP IS PERFORMED. THE OUTLINED
С
      SEQUENCE IS REPEATED 9 TIMES TO CONVERGE ON AN APPROPRIATE
С
      DESIGN PARAMETER. THIS ITERATION IS DONE IN SUBROUTINE
C
      "NEWTON" WHICH CALLS FUNCTION SUBPROGRAMS "FCN" AND "FDER"
С
      TO CALCULATE THE OBJECTIVE FUNCTION AND ITS DERIVATIVE,
Ċ
      RESPECTIVELY. CONVERGENCE IS ACHIEVED WHEN
```

С 1) THE OBJECTIVE FUNCTION IS LESS THAN OR EQUAL TO 1.D-04 OR С 2) THE RELATIVE ERROR FOR SUCCESSIVE ITERATIONS IN THE DESIGN С PARAMETER IS LESS THAN OR EQUAL TO 1.D-06. С C----THE NECESSARY INPUT DATA ARE:-----Ċ С TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С С ---SOLUTION PROPERTIES---С С MUF - FLUID VISCOSITY, CP - FLUID-PHASE DENSITY, G/CM\*\*3 С RHOF С DF - FLUID-PHASE DIFFUSIVITY, CM\*\*2/SEC С С ---SOLID SORBENT PROPERTIES---С С ĸ - ADSORPTION EQUILIBRIUM CONSTANT, UNITLESS С Q0 - SOLID SORBENT LIGAND CAPACITY, MG/G RESIN С - EFFECTIVE PARTICLE-PHASE DIFFUSIVITY OF LIGAND, DP С CM\*\*2/SEC С D - DIAMETER OF SOLID PARTICLES, CM С С ---FIXED BED PROPERTIES---С С RHOB - BULK DENSITY OF BED, G/CM\*\*3 С BETA - FRACTIONAL VOIDAGE IN BED, CM\*\*3 VOID/CM\*\*3 BED С DB - BED DIAMETER, CM С С ----RUN PARAMETERS---С С TEMP - COLUMN TEMPERATURE, C C C0 - FEED CONCENTRATION FOR LIGAND SORPTION, MG/CM\*\*3 С С - DESIRED CONCENTRATION FOR DESIGNED BED LENGTH OR С BREAKTHROUGH TIME, MG/CM\*\*3 QRATE - VOLUMETRIC FLOW RATE, CM\*\*3/SEC С NUMRAT - NUMBER DESCRIBING KINETIC DRIVING FORCE EXPRESSION С С F(C,Q) AS FOLLOWS С C NUMRAT FORWARD REVERSE 1 COMMENT L С RATE ORDER RATE ORDER 1 С С С 1 2 2 С С 2 2 1 LANGMUIR С KINETICS С 3 2 0 E C С 4 | FILM RESISTANCE 1 1 C CONTROLLING 1 С 5 1 1 0 | INDEPENDENT OF

С TIME С I 6 1 1 DIFFUSION С CONTROLLING С C ILT - NUMBER DESCRIBING DESIGN OPTION C = 1 BED LENGTH С = 2 BREAKTHROUGH TIME С TVAL - REAL TIME VALUE GREATER THAN BED RESIDENCE TIME, SEC C (FOR ILT = 2, THIS IS A GUESS VALUE) С Z - BED LENGTH, CM С (FOR ILT = 1, THIS IS A GUESS VALUE) С C----THE CALCULATED VALUES ARE:-----С Ç U - SUPERFICIAL FLUID VELOCITY, CM/SEC С Ċ RESTIM - BED RESIDENCE TIME, SEC С С H - FLUID-PHASE MASS TRANSFER COEFFICIENT, CM/SEC С С - KINETIC PARAMETER, UNITS VARY KVAL С CM\*\*3 FLUID/(SEC\*MG) FOR NUMRAT = 1 THRU 5 C 1/SEC FOR NUMRAT = 6 С С - DIMENSIONLESS LENGTH OR NUMBER OF TRANSFER Ν С UNITS С С R - SEPARATION FACTOR, UNITLESS C С VCOL - VOLUMETRIC THROUGHPUT, CM\*\*3 С С NT - DIMENSIONLESS TIME С C т - THROUGHPUT PARAMETER, UNITLESS С С X - DIMENSIONLESS CONCENTRATION С С С READ THE TITLE OF THE SYSTEM TO BE STUDIED. C READ (5,111) TITLE 111 FORMAT (A60) C C READ THE SOLUTION PROPERTIES. С READ (5,\*) MUF, RHOF, DF С С READ THE SOLID SORBENT PROPERTIES. С READ (5,\*) K,Q0,DP,D С

```
С
      READ THE FIXED BED PROPERTIES.
С
      READ (5,*) RHOB, BETA, DB
С
С
      READ THE RUN PARAMETERS, CALCULATE THE SUPERFICIAL VELOCITY
С
      AND CALCULATE A TERM USED IN THE OBJECTIVE FUNCTION (THE
      OBJECTIVE FUNCTION IS CALCULATED IN SUBPROGRAM FCN).
С
C
    READ (5,*) TEMP, CO, C, ORATE, NUMRAT, ILT, TVAL, Z
      U = QRATE/(7.853981634D-01*DB**2)
      X = C/CO
      TERM2 = DLOG(X)
      TERM3 = DLOG(1.DO/X - 1.DO)
С
С
      WRITE THE HEADING AND THE INPUT DATA (AS A CHECK).
С
      WRITE (6,10)
   10 FORMAT(1H1,12X, 'DESIGN OF A LIGAND EXCHANGE COLUMN BY'./.21X.
     1'THE THOMAS MODEL')
     WRITE (6,11) TITLE
   11 FORMAT(///,1X,A60)
      WRITE (6,12)
   12 FORMAT(////,3X,'THE INPUT DATA ARE AS FOLLOWS:'//)
      WRITE (6,13) MUF
   13 FORMAT(/' THE FLUID-PHASE VISCOSITY IS ',1PD12.5,' CP')
      WRITE (6,14) RHOF
   14 FORMAT(/' THE FLUID-PHASE DENSITY IS ',1PD12.5,' G/CM**3')
      WRITE (6,15) DF
   15 FORMAT(/' THE FLUID-PHASE DIFFUSIVITY IS '.1PD12.5.' CM**2/SEC')
     WRITE (6,16) K
   16 FORMAT(/' THE ADSORPTION EQUILIBRIUM CONSTANT IS', 1PD12.5)
     WRITE (6,17) QO
   17 FORMAT(/' THE SORBENT LIGAND CAPACITY IS ', 1PD12.5, ' MG/G RESIN')
     WRITE (6,18) DP
  18 FORMAT(/' THE EFFECTIVE PARTICLE-PHASE DIFFUSIVITY IS ',1PD12.5,
     1' CM**2/SEC')
     WRITE (6,19) D
  19 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
     WRITE (6,20) RHOB
  20 FORMAT(/' THE BULK BED DENSITY IS ',1PD12.5,' G/CM**3')
     WRITE (6,21) BETA
  21 FORMAT(/' THE FRACTIONAL BED VOIDAGE IS ',1PD12.5,' CM**3 VOID/CM
    1**3 BED')
     WRITE (6,22) DB
  22 FORMAT(/' THE BED DIAMETER IS ',1PD12.5,' CM')
     WRITE (6,23) TEMP
  23 FORMAT(/' THE COLUMN TEMPERATURE IS ',1PD12.5,' C')
     WRITE (6,24) CO
  24 FORMAT(/' THE FEED CONCENTRATION FOR LIGAND SORPTION IS ', 1PD12.5
    1,' MG/CM**3')
     WRITE (6,25) C
  25 FORMAT(/' THE DESIRED CONCENTRATION IS ',1PD12.5,' CM')
```

```
WRITE (6,26) QRATE
   26 FORMAT(/: THE VOLUMETRIC FLOW RATE IS '.1PD12.5,' CM**3/SEC')
      WRITE (6,27) NUMRAT
   27 FORMAT(/' THE KINETIC EXPRESSION DESCRIBING THE NET COMPLEXING',
     1/.' RATE IS REACTION NUMBER'.I2)
      IF (ILT .EQ. 1) THEN
      WRITE (6,28) TVAL,Z
   28 FORMAT(//' DESIGN OF AN APPROPRIATE BED LENGTH',/,' THE REQUIR
     1ED BREAKTHROUGH TIME IS ',1PD12.5,' SEC',/,' THE INITIAL-GUESS BE
     2D LENGTH IS ',1PD12.5,' CM')
      ELSE
      WRITE (6,29) TVAL,Z
   29 FORMAT(//'
                   DESIGN OF AN APPROPRIATE BREAKTHROUGH TIME',/,' THE
     1 INITIAL-GUESS BREAKTHROUGH TIME IS ',1PD12.5,' SEC',/,' THE REQU
     2IRED BED LENGTH IS ',1PD12.5,' CM')
      END IF
C
С
      THE KINETIC EXPRESSION CORRESPONDING TO NUMRAT = 5 GIVES
С
      A MODEL WITH NO FUNCTIONAL DEPENDENCE ON TIME. THEREFORE,
С
      WHEN NUMRAT = 5 AND ILT = 2 AN ERROR MESSAGE IS GIVEN.
С
      IF (ILT .EQ. 2 .AND. NUMRAT .EQ. 5) THEN
      WRITE (6,999)
  999 FORMAT(//,5X,'THE DESIRED MODEL IS NOT A FUNCTION OF TIME')
      ELSE
      RESTIM = Z*BETA/U
        IF (TVAL .LT. RESTIM) THEN
        WRITE(6,998)
  998 FORMAT(//.5X, 'THE INPUT TIME VALUE IS TOO SMALL')
        ELSE
Ç
С
      THE KINETIC PARAMETER IS CALCULATED BY SUBROUTINE KINET.
C
      CALL KINET(D, RHOB, DP, K, CO, U, BETA, QO, NUMRAT, H, KVAL, IFLG1)
       IF (IFLG1 .EQ. -1) THEN
С
C
        WRITE(6,997)
C 997 FORMAT(/,' THE J-FACTOR CORRELATION IS NOT APPROPRIATE; THE FLOWR
С
     1ATE IS TOO HIGH')
С
       ELSE
С
С
      HERE, THE DERIVATIVE OF THE DIMENSIONLESS TIME WITH
C
      RESPECT TO THE BED LENGTH IS CALCULATED. AFTERWARDS,
      THE DERIVATIVE OF THE DIMENSIONLESS TIME WITH RESPECT
С
      TO TIME IS EASILY OBTAINED. THESE VALUES ARE USED IN
C
С
      FUNCTION SUBPROGRAM "FDER."
C
              DNTDZ = DDZ(KVAL, CO, BETA, U, K, NUMRAT)
              DNTDT = - DNTDZ*U/BETA
С
С
      THE SEPARATION FACTOR IS CALCULATED BY FUNCTION SEPRTE.
С
              R = SEPRTE(K, NUMRAT)
```

```
С
С
      SET CONVERGENCE CRITERIA ON TVAL OR Z.
C
              TOL = 1.D-06
              NITER = 20
              NACL = 10
С
С
      SUBROUTINE NEWTON IS CALLED TO DETERMINE THE OPTIMUM
С
      DESIGN LENGTH OR BREAKTHROUGH TIME.
С
                   IF (ILT .EQ. 1) THEN
                   CALL NEWTON(Z,ZERO,TOL,NITER,NACL, IFLG)
                   ELSE
Ĉ
С
      THE DIMENSIONLESS LENGTH IS CALCULATED BY FUNCTION LNGTH.
С
      FOR ILT = 1, THE VALUE OF N WILL REMAIN CONSTANT.
С
                   N = LNGTH(KVAL, RHOB, QO, CO, Z, U, NUMRAT)
                   CALL NEWTON(TVAL, ZERO, TOL, NITER, NACL, IFLG)
.
                   END IF
С
С
         IF (IFLG .EQ. 0) THEN
С
С
      CALCULATE THE VOLUMETRIC THROUGHPUT AND THE THROUGHPUT
С
      PARAMETER.
С
         VCOL = QRATE*TVAL
         T = NT/N
С
      BEGIN WRITING THE OUTPUT DATA. WRITE THE NUMBER OF TRANSFER
С
С.
      UNITS AND THE SEPARATION FACTOR.
С
      WRITE (6,30) H
   30 FORMAT(1H1,3X,'THE CALCULATED VALUES ARE:',///,' THE FLUID-PHASE
     1MASS TRANSFER COEFFICIENT IS ',1PD12.5,' CM/SEC')
      WRITE (6,31) N
   31 FORMAT(/,' THE NUMBER OF TRANSFER UNITS IS ',1PD12.5)
      WRITE (6,32) R
   32 FORMAT(/,' THE SEPARATION FACTOR IS ',1PD12.5)
      WRITE (6,33) RESTIM
   33 FORMAT(/,' THE BED RESIDENCE TIME IS ',1PD12.5,' SEC')
         WRITE (6,34) T
   34 FORMAT(/,' THE THROUGHPUT PARAMETER IS ',1PD12.5)
         WRITE (6,35) VCOL
   35 FORMAT(/, ' THE VOLUME OF FLUID TREATED IS ',1PD12.5,' CM**3')
         WRITE (6,36) NT
   36 FORMAT(/,' THE DIMENSIONLESS TIME IS ',1PD12.5)
         WRITE (6,37) X
   37 FORMAT(/,' THE DIMENSIONLESS CONCENTRATION IS ',1PD12.5)
          IF (ILT .EO. 1) THEN
          WRITE (6,38) Z
```

```
FORMAT(//, ' THE DESIGN BED LENGTH IS ', 1PD12.5, ' CM')
   38
         ELSE
         WRITE (6,39) TVAL
         FORMAT(//,' THE DESIGN BREAKTHROUGH TIME IS ',1PD12.5,' SEC')
   39
         END IF
     WRITE (6,40) ZERO
   40 FORMAT(//,' THE OBJECTIVE FUNCTION WAS MINIMIZED TO ', 1PD12.5)
        ELSE
        IF (IFLG .EQ. 1) WRITE (6,41)
        IF (IFLG .EQ. 2) WRITE (6,42)
        IF (IFLG .EQ. 3) WRITE (6,43)
        IF (IFLG .EQ. 4) WRITE (6,44)
  41 FORMAT(//,1X, ' CONVERGENCE WAS NOT ACHIEVED IN THE GIVEN NUMBER',/
    1.1X.' OF ITERATION AND ACCELERATION STEPS')
  42 FORMAT(//,1X,' THE ITERATION PROCEDURE PRODUCED A NEGATIVE ROOT')
  43 FORMAT(//,1X,' A LOCAL MAXIMUM OR MINIMUM HAS BEEN ENCOUNTERED',/,
    11X, ' THE INITIAL-GUESS VALUE IS POSSIBLY TOO FAR FROM THE ACTUAL V
    2ALUE ')
  44 FORMAT(//,1X,' THE DIMENSIONLESS TIME BECAME NEGATIVE DURING THE I
    1TERATION')
        END IF
       END IF
С
      END IF
     END IF
     STOP
     END
С
     FUNCTION DDZ(KVAL, CO, BETA, U, K, NUMRAT)
     IMPLICIT REAL*8 (A-H,O-Z)
     DOUBLE PRECISION K, KVAL
С
C---
            С
С
      THIS SUBPROGRAM CALCULATES THE DERIVATIVE OF THE DIMENSION-
     LESS TIME WITH RESPECT TO THE BED LENGTH. THIS VALUE IS A
C
С
     FUNCTION OF THE DESIRED RATE EXPRESSION (VIA NUMRAT VALUE).
C
C
     DDZ = - KVAL*BETA/U
     IF (NUMRAT .GE. 5) GO TO 1
     DDZ = DDZ*CO
     IF (NUMRAT .EQ. 2) DDZ = DDZ^{*}(1.D0 + 1.D0/K)
     GO TO 2
   1 IF (NUMRAT .EQ. 5) DDZ = 0.D0
   2 RETURN
     END
С
     SUBROUTINE NEWTON (XN, FCT, XTOL, NITER, NACL, IFLG)
C..........
С
С
     PURPOSE
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С TO SOLVE GENERAL NONLINEAR EQUATIONS OF THE FORM FCN(X)=0 С BY MEANS OF NEWTON-RHAPSON ITERATION METHOD. C С USAGE С CALL NEWTON(XN, FCT, XTOL, NITER, NACL, IFLG) С C DESCRIPTION OF PARAMETERS С XN - DOUBLE PRECISION RESULTANT ROOT OF EQUATION C FCT(X)=0. С FCT - DOUBLE PRECISION RESULTANT FUNCTION VALUE С AT ROOT X. С XTOL - DOUBLE PRECISION INPUT VALUE WHICH SPECIFIES THE C UPPER BOUND OF THE RELATIVE ERROR OF RESULT X. С NITER - MAXIMUM NUMBER OF ITERATION STEPS SPECIFIED. С NACL - NUMBER OF WEGSTEIN ACCELERATION STEPS SPECIFIED. С IFLG - RESULTANT ERROR PARAMETER CODED AS FOLLOWS С IFLG=0 - NO ERROR. C IFLG=1 - NO CONVERGENCE AFTER NITER ITERATION С STEPS FOLLOWED BY NACL ACCELERATION C STEPS. C IFLG=2 - NEGATIVE ROOT OBTAINED С IFLG=3 - LOCAL MAXIMUM OR MINIMUM ENCOUNTERED С С С С REMARKS С THIS PROCEDURE UTILIZES THE WELL-KNOWN NEWTON-RHAPSON С TECHNIQUE FOR CONVERGENCE ON A ROOT. IF THE ROOT С XN GOES NEGATIVE AT ANY TIME, THE PROCEDURE IS BYPASSED AND AN ERROR MESSAGE OCCURS, IFLG = 2. С С С SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED С FCN - DOUBLE PRECISION FUNCTION SUBPROGRAM WHICH С CALCULATES THE FUNCTION TO BE ZEROED. С FDER - DOUBLE PRECISION FUNCTION SUBPROGRAM WHICH С CALCULATES THE DERATIVE OF THE AFOREMENTIONED С FUNCTION. С С METHOD С SOLUTION OF EQUATION FCN(X)=0 IS DONE BY MEANS OF С A NEWTON-RHAPSON CONVERGENCE SCHEME. THE STARTING VALUE Ċ FOR THE ITERATION IS THE INPUT VALUE XN. THE CONVERGENCE C CRITERIA IS ABS((XN1-XN)/XN) .LE. XTOL OR FCN(X) .LE. С 100.\*XTOL. IF THE REQUIRED CONVERGENCE ON A NON-NEGATIVE С XN IS NOT ACHIEVED WITHIN NITER ITERATIONS, THEN A WEGSTEIN С ACCELERATION IS USED (UP TO NACL TIMES). FOR A DESCRIPTION С OF THE WEGSTEIN METHOD SEE С С WEGSTEIN, J.H., "COMM .ASSN. OF COMPUTING MACHINERY, "1(9), 1958. С Ċ 

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IMPLICIT REAL*8 (A-H,O-Z)
      DOUBLE PRECISION N,NT
      COMMON /PARAM2/DNTDZ, DNTDT, NUMRAT, ILT, Z, TVAL, N, NT, R, BETA, U
      NLESS = NITER - 1
      FTOL = 100.D0*XTOL
         DO 1 J=1,NACL
            DO 2 K=1,NITER
            IF (XN .LT. 0.) GO TO 6
            FCT = FCN(XN)
            IF (NT .LT. 0.D0) GO TO 4
            DFCT = FDER(XN)
            IF (DABS(DFCT) .LE. 1.D-60) GO TO 3
            XN1 = XN - FCT/DFCT
            IF (DABS((XN1-XN)/XN) .LE. XTOL .OR. DABS(FCT) .LE. FTOL)
     *
            GO TO 5
            IF (K .EQ. NLESS) DN = DABS(FCT)
            XN = XN1
    2
            CONTINUE
         DN1 = DABS(FCT)
         Q = DN/(DN - DN1)
         XN = Q^*XN1 + (1.D0 - Q)^*XN
         CONTINUE
    1
      IF (DABS((XN1-XN)/XN) .LE. XTOL .OR. DABS(FCT) .LE. FTOL) GO TO 5
      IFLG = 1
      GO TO 7
    3 IFLG = 3
      GO TO 7
    4 IFLG = 4
      GO TO 7
    5 \text{ IFLG} = 0
      GO TO 7
    6 IFLG = 2
    7 RETURN
      END
      FUNCTION PHI2(U,V)
      IMPLICIT REAL*8 (A-H,O-Z)
                                  -
C-----
                                       -----
      PROGRAMMER: WAYNE BOLDEN
                                     MARCH 7, 1985
       THIS SUBPROGRAM CALCULATES REPRESENTATIVE VALUES OF THE
      DERIVATIVE OF THE J-FUNCTION WITH RESPECT TO THE SECOND
      ARGUMENT "V." THE RELEVANT EQUATIONS AND EXPLANATIONS ARE
      GIVEN IN THE FOLLOWING SOURCES:
      1) TAN, H.K.S., 'CHEM. ENG.,' DEC. 24, 1984, 57.
      2) SHERWOOD, T.K., ET AL., "MASS TRANSFER," MCGRAW-HILL,
        NEW YORK (1975), 567.
```

С С 3) LIAW, C.H., ET AL., 'AICHE J.,' VOL. 25, NO. 2, 1979, 376. С C--\_\_\_\_\_ С С IF EITHER U OR V IS LESS THAN OR EQUAL TO 1.D-02, THE С PHI2 FUNCTION VALUE IS SET TO 0.DO. С IF (U .LE. 1.D-02 .OR. V .LE. 1.D-02) GO TO 2 С С IF EITHER OF THE ARGUMENTS IS GREATER THAN 10., AN С APPROXIMATION OF THE PHI2 FUNCTION IS USED. С IF (U .GT. 10.DO .OR. V .GT. 10.DO) GO TO 3 С С IF EITHER VALUE IS A FACTOR OF 20 GREATER THAN THE OTHER, С THEN THE VALUE OF SMALLER ARGUMENT IS TAKEN TO BE ZERO. С IF (U/V .GT. 20.D0 .OR. V/U .GT. 20.D0) GO TO 2 С С OTHERWISE, THE MORE EXACT LOGARITHMIC EXPANSION IS USED. Ċ DUBU = 2.\*UDUBV = 2.\*VD = DMAX1(DUBU, DUBV)N = 20 + IDINT(D)DBK = 0.D0SUM2 = 0.D0BIGSUM = 0.D0DO 1 K =1,N RK = KSUM1 = SUM2SUM2 = SUM2 + DLOG(RK)ARG1 = (RK - 1.D0)\*DLOG(V) - V - SUM1ARG2 = RK\*DLOG(U) - U - SUM2IF (ARG1 .LT. -174.D0) ARG1 = -174.D0 IF (ARG2 .LT. -174.D0) ARG2 = -174.D0 IF (ARG1 .GT. 174.D0) ARG1 = 174.D0 IF (ARG2 .GT. 174.D0) ARG2 = 174.D0 DBK = DBK + (1.D0 - (RK - 1.D0)/V)\*DEXP(ARG1)BIGSUM = BIGSUM + DBK\*DEXP(ARG2)1 PHI2 = BIGSUM GO TO 4 2 PHI2 = 0.00GO TO 4 С С IF EITHER VALUE IS A FACTOR OF 20 GREATER THAN THE OTHER, Ċ THEN THE VALUE OF SMALLER ARGUMENT IS TAKEN TO BE ZERO. С 3 IF (U/V .GT. 20.DO .OR. V/U .GT. 20.DO) GO TO 31 ARG3 = DSQRT(U) - DSQRT(V)

С

```
С
      NUMERICAL OVERFLOW CAN OCCUR IN THE APPROXIMATIONS
С
      WHEN DABS(ARG3) IS GREATER THAN 13.2 .
C
      IF (DABS(ARG3) .GT. 13.2D0) GO TO 31
      RTPI2 = 3.544907702D0
      DENOM = DSQRT(V) + (U*V)**0.25
      FACTOR = 1.D0 + ARG3/DENOM - (0.5D0 + 0.25D0*(U/V)**0.25)/DENOM**2
      PHI2 = DEXP(-ARG3**2)*FACTOR/(DSORT(V)*RTPI2)
      GO TO 4
   31 \text{ PHI2} = 0.00
    4 RETURN
      END
C
      FUNCTION FCN(ZORT)
      IMPLICIT REAL*8 (A-H.O-Z)
     DOUBLE PRECISION JFUNC, LNGTH, N, NT, K, KVAL, NUMER
     COMMON /PARAM1/K, KVAL, CO, OO, RHOB, TERM2, TERM3
     COMMON /PARAM2/DNTDZ, DNTDT, NUMRAT, ILT, Z, TVAL, N, NT, R, BETA, U
С
C
С
       THIS SUBPROGRAM CALCULATES THE OBJECTIVE FUNCTION TO BE
С
     USED IN OBTAINING THE OPTIMUM DESIGN PARAMETER. IT IS A
      FUNCTION OF THE DESIGN OPTION (SPECIFIED BY ILT = 1 \text{ OR } 2)
С
С
     AND THE DESIRED RATE EXPRESSION (DEFINED BY THE NUMRAT VALUE).
C
C-----
С
     IF (ILT .EQ. 1) THEN
     Z = ZORT
     N = LNGTH(KVAL, RHOB, Q0, C0, Z, U, NUMRAT)
     NT = TIME(KVAL, CO, TVAL, Z, BETA, U, K, NUMRAT)
     IF (NT .LT. 0.D0) RETURN
     ELSE
     TVAL = ZORT
     NT = TIME(KVAL,CO,TVAL,Z,BETA,U,K,NUMRAT)
     IF (NT .LT. 0.DO) RETURN
     END IF
С
     IF (NUMRAT .GE. 3) THEN
        IF (NUMRAT .EQ. 4 .OR. NUMRAT .EQ. 6) THEN
С
     THIS IS WHERE CALCULATIONS ARE MADE FOR REACTION RATE
Ç
С
     EXPRESSION 4 OR 6.
C
        ARGLOG = JFUNC(N,NT)
           IF (ARGLOG .LE. 1.D-60) THEN
           FCN = -1.40D+02
           ELSE
           FCN = DLOG(ARGLOG) - TERM2
           END IF
        ELSE
```

С С THE CALCULATIONS ARE MADE FOR REACTION RATE EXPRESSION C 3 OR 5. C IF (N .GT. 174.D0) THEN FCN = N - TERM3ELSE ARGLOG = 1.DO - DEXP(-N)FCN = N + DLOG(ARGLOG) - TERM3END IF IF (NUMRAT .EQ. 3) FCN = FCN - NTEND IF ELSE IF (NT .GT. 10.DO .OR. N .GT. 10.DO) THEN C С CALCULATIONS ARE MADE FOR LARGE ARGUMENT VALUES С USING REACTION RATE EXPRESSION 1 OR 2. C RTPI = 1.772453851D0CONST = 1.265512123D0ARGN = DSQRT(R\*NT) - DSQRT(N)ARGD = DSQRT(R\*N) - DSQRT(NT)TRMN = 1.DO/((R\*N\*NT)\*\*0.25 + DSORT(R\*NT))TRMD = 1.DO/((R\*N\*NT)\*\*0.25 + DSQRT(NT))IF (ARGN .LT. -7.DO .OR. ARGD .LT. -7.DO) THEN IF (ARGN .LT. -7.DO .AND. ARGD .LT. -7.DO) THEN Ċ С THE OBJECTIVE FUNCTION IS CALCULATED WITH SIMPLIFICATIONS С INCLUDED FOR ARGN < -7 AND ARGD < -7. С FCN = (R - 1.D0)\*(NT - N) - TERM3. ELSE IF (ARGN .LT. -7.DO) THEN IF (DABS(ARGD) .LT. 7.DO) THEN С С THE OBJECTIVE FUNCTION IS CALCULATED FOR ARGN < -7 AND Ç |ARGD| < 7.С VALD = RTPI\*(DERFC(ARGD))\*DEXP(ARGD\*\*2) DENOM = VALD + TRMDFCN = CONST + ARGN\*\*2 - DLOG(DENOM) - TERM3ELSE С С THE OBJECTIVE FUNCTION IS CALCULATED FOR ARGN < -7 AND С ARGD > 7.C FCN = CONST + ARGN\*\*2 + DLOG(ARGD) - TERM3END IF ELSE IF (DABS(ARGN) .LT. 7.D0) THEN С С THE OBJECTIVE FUNCTION IS CALCULATED FOR [ARGN] < 7 AND

```
С
      ARGD < -7.
С
                    VALN = RTPI*(DERFC(ARGN))*DEXP(ARGN**2)
                   NUMER = VALN - TRMN
                    FCN = -CONST - ARGD^{**2} + DLOG(NUMER) - TERM3
                  ELSE
С
С
      THE OBJECTIVE FUNCTION IS CALCULATED FOR ARGN > 7 AND
С
      ARGD < -7.
С
                   FCN = -CONST - ARGD**2 - DLOG(ARGN) - TERM3
                   END IF
                 END IF
            END IF
          ELSE
             IF (ARGN .GT. 7.DO .OR. ARGD .GT. 7.DO) THEN
                    IF (ARGN .GT. 7.DO .AND. ARGD .GT. 7.DO) THEN
С
С
      THE OBJECTIVE FUNCTION IS CALCULATED FOR ARGN > 7 AND
C
      ARGD > 7.
С
                    FCN = - DLOG(ARGN) + DLOG(ARGD) - TERM3
                    ELSE
                        IF (ARGN .GT. 7.DO) THEN
Ç
С
      THE OBJECTIVE FUNCTION IS CALCULATED FOR ARGN > 7 AND
С
      |ARGD| < 7.
С
                       VALD = RTPI*(DERFC(ARGD))*DEXP(ARGD**2)
                       DENOM = VALD + TRMD
                       FCN = - DLOG(ARGN) - DLOG(DENOM) - TERM3
                       ELSE
С
С
      THE OBJECTIVE FUNCTION IS CALCULATED FOR |ARGN| < 7 AND
С
      ARGD > 7.
С
                       VALN = RTPI*(DERFC(ARGN))*DEXP(ARGN**2)
                       NUMER = VALN - TRMN
                       FCN = DLOG(NUMER) + DLOG(ARGD) - TERM3
                       END IF
                    END IF
             ELSE
С
С
      THE OBJECTIVE FUNCTION IS CALCULATED FOR |ARGN| < 7 AND
С
      |ARGD| < 7.
С
             VALN = RTPI*(DERFC(ARGN))*DEXP(ARGN**2)
             VALD = RTPI*(DERFC(ARGD))*DEXP(ARGD**2)
             NUMER = VALN - TRMN
             DENOM = VALD + TRMD
             FCN = DLOG(NUMER) - DLOG(DENOM) - TERM3
             END IF
```

```
END IF
       ELSE
С
С
     THE APPROPRIATE CALCULATIONS ARE MADE FOR SMALL ARGUMENT
С
     VALUES USING REACTION RATE EXPRESSION 1 OR 2.
С
       ARGLOG = JFUNC(R*N.NT)
       IF (ARGLOG .LT. 1.D-60) ARGLOG = 1.D-60
       FACTOR = JFUNC(R*NT,N)
       IF (FACTOR .LT. 1.D-60) FACTOR = 1.D-60
       PHI1 = FACTOR^{(1.D0 - PHI0(R^{NT},N)/FACTOR)}
       FCN = DLOG(PHI1) - DLOG(ARGLOG) + (R - 1.D0)*(NT - N) - TERM3
       END IF
     END IF
   99 RETURN
     END
С
     FUNCTION FDER(ZORT)
     IMPLICIT REAL*8 (A-H,O-Z)
     DOUBLE PRECISION JFUNC, N, NT, NUMER
     COMMON /PARAM2/DNTDZ, DNTDT, NUMRAT, ILT, Z, TVAL, N, NT, R, BETA, U
С
С
C
      THIS SUBPROGRAM CALCULATES THE OBJECTIVE FUNCTION DERI-
     VATIVE USED IN OBTAINING THE OPTIMUM DESIGN PARAMETER. IT
С
С
     IS ALSO A FUNCTION OF THE DESIGN OPTION AND THE DESIRED
C
     RATE EXPRESSION.
С
C______
С
     IF (NUMRAT .GE. 3) THEN
        IF (NUMRAT .EQ. 4 .OR. NUMRAT .EQ. 6) THEN
С
Ċ
     THIS IS WHERE CALCULATIONS ARE MADE FOR REACTION RATE
С
     EXPRESSION 4 OR 6.
С
        FCTR = JFUNC(N,NT)
        IF (FCTR .LT. 1.D-60) FCTR = 1.D-60
          IF (ILT .EQ. 1) THEN
          TERM = DNTDZ*PHI2(N,NT) - N*PHIO(N,NT)/Z
          ELSE
          TERM = DNTDT*PHI2(N,NT)
          END IF
        FDER = TERM/FCTR
        ELSE
С
С
     THE CALCULATIONS ARE MADE FOR REACTION RATE EXPRESSION
С
     3 OR 5.
С
           IF (ILT .EQ. 1) THEN
                IF (N .GT. 174.DO) THEN
```

```
FDER = N/Z - DNTDZ
                  ELSE
                  FDER = N/((1.D0 - DEXP(-N))*Z) - DNTDZ
                  END IF
            ELSE
            FDER = - DNTDT
            END IF
         IF (NUMRAT .EQ. 5) FDER = FDER + DNTDZ
         END IF
      ELSE
        IF (NT .GT. 10.DO .OR. N .GT. 10.DO) THEN
С
С
      CALCULATIONS ARE MADE FOR LARGE ARGUMENT VALUES
С
      USING REACTION RATE EXPRESSION 1 OR 2.
С
        RTPI = 1.772453851D0
        ARGN = DSQRT(R*NT) - DSQRT(N)
        ARGD = DSQRT(R*N) - DSQRT(NT)
        TRMN = 1.DO/((R*N*NT)**0.25 + DSQRT(R*NT))
        TRMD = 1.DO/((R*N*NT)**0.25 + DSQRT(NT))
           IF (ILT .EQ. 1) THEN
           D2ARGN = DSQRT(R/NT)*DNTDZ - DSQRT(N)/Z
           BRAC2N = (0.5D0*DSQRT(R/NT) + 0.25D0*(R*N/NT**3)**0.25)*DNTDZ
                    + 0.25D0*(R*N*NT)**0.25/Z
     1
           D2ARGD = DSQRT(R*N)/Z - DNTDZ/DSQRT(NT)
           BRAC2D = (0.5DO/DSQRT(NT) + 0.25DO*(R*N/NT**3)**0.25)*DNTDZ
                    + 0.25D0*(R*N*NT)**0.25/Z
     1
           ELSE
           D2ARGN = DSORT(R/NT)*DNTDT
           BRAC2N = (0.5D0*DSQRT(R/NT) + 0.25D0*(R*N/NT**3)**0.25)*DNTDT
           D2ARGD = - DNTDT/DSQRT(NT)
           BRAC2D = (0.5DO/DSQRT(NT) + 0.25DO*(R*N/NT**3)**0.25)*DNTDT
           END IF
          IF (ARGN .LT. -7.DO .OR. ARGD .LT. -7.DO) THEN
            IF (ARGN .LT. -7.DO .AND. ARGD .LT. -7.DO) THEN
С
С
      THE FUNCTION DERIVATIVE IS CALCULATED WITH SIMPLIFICATIONS
С
      INCLUDED FOR ARGN < -7 AND ARGD < -7.
С
            FDER \doteq (R - 1.D0)*DNTDT
            IF (ILT .EQ. 1) FDER = (R - 1.D0)*(DNTDZ - N/Z)
            ELSE
                 IF (ARGN .LT. -7.DO) THEN
                   IF (DABS(ARGD) .LT. 7.DO) THEN
С
С
      THE FUNCTION DERIVATIVE IS CALCULATED FOR ARGN < -7 AND
С
      |ARGD| < 7.
С
                   VALD = RTPI*(DERFC(ARGD))*DEXP(ARGD**2)
                   DENOM = VALD + TRMD
                   DDENOM = (VALD*ARGD - 1.D0)*D2ARGD - BRAC2D*TRMD**2
                   FDER = ARGN*D2ARGN - DDENOM/DENOM
```

ELSE С С THE FUNCTION DERIVATIVE IS CALCULATED FOR ARGN < -7 AND С ARGD > 7. С FDER = ARGN\*D2ARGN + D2ARGD/(2.D0\*ARGD)END IF ELSE IF (DABS(ARGN) .LT. 7.DO) THEN С THE FUNCTION DERIVATIVE IS CALCULATED FOR |ARGN| < 7 AND С С ARGD < -7. С  $VALN = RTPI^{(DERFC(ARGN))^{DEXP(ARGN^{2})}$ NUMER = VALN - TRMN DNUMER = (VALN\*ARGN - 1.D0)\*D2ARGN + BRAC2N\*TRMN\*\*2 FDER = DNUMER/NUMER - ARGD\*D2ARGD ELSE С THE FUNCTION DERIVATIVE IS CALCULATED FOR ARGN > 7 AND С ARGD < -7. Ċ С FDER = - ARGD\*D2ARGD - D2ARGN/(2.D0\*ARGN)END IF END IF END IF ELSE IF (ARGN .GT. 7.DO .OR. ARGD .GT. 7.DO) THEN IF (ARGN .GT. 7.DO .AND. ARGD .GT. 7.DO) THEN С С THE FUNCTION DERIVATIVE IS CALCULATED FOR ARGN > 7 AND С ARGD > 7.С FDER = 0.5D0\*(- D2ARGN/ARGN + D2ARGD/ARGD)ELSE IF (ARGN .GT. 7.DO) THEN С THE FUNCTION DERIVATIVE IS CALCULATED FOR ARGN > 7 AND С С |ARGD| < 7.С VALD = RTPI\*(DERFC(ARGD))\*DEXP(ARGD\*\*2) DENOM = VALD + TRMDDDENOM = (VALD\*ARGD - 1.D0)\*D2ARGD - BRAC2D\* 1 TRMD\*\*2 FDER = - D2ARGN/(2.D0\*ARGN) - DDENOM/DENOMELSE С С THE FUNCTION DERIVATIVE IS CALCULATED FOR |ARGN| < 7 AND С ARGD > 7. С VALN = RTPI\*(DERFC(ARGN))\*DEXP(ARGN\*\*2)NUMER = VALN - TRMN

```
DNUMER = (VALN*ARGN - 1.DO)*D2ARGN + BRAC2N*
     1
                                 TRMN**2
                       FDER = DNUMER/NUMER + D2ARGD/(2.D0*ARGD)
                       END IF
                    END IF
             ELSE
C
С
      THE FUNCTION DERIVATIVE IS CALCULATED FOR [ARGN] < 7 AND
С
      |ARGD| < 7.
С
             VALN = RTPI*(DERFC(ARGN))*DEXP(ARGN**2)
             VALD = RTPI*(DERFC(ARGD))*DEXP(ARGD**2)
             NUMER = VALN - TRMN
             DENOM = VALD + TRMD
             DNUMER = (VALN*ARGN - 1.D0)*D2ARGN + BRAC2N*TRMN**2
             DDENOM = (VALD*ARGD - 1.D0)*D2ARGD - BRAC2D*TRMD**2
             FDER = DNUMER/NUMER - DDENOM/DENOM
             END IF
          END IF
        ELSE
С
С
      THE APPROPRIATE CALCULATIONS ARE MADE FOR SMALL ARGUMENT
С
      VALUES USING REACTION RATE EXPRESSION 1 OR 2.
С
        VAL1 = JFUNC(R*N,NT)
        IF (VAL1 .LT. 1.D-60) VAL1 = 1.D-60
        FACTOR = JFUNC(R*NT,N)
        IF (FACTOR .LT. 1.D-60) FACTOR = 1.D-60
        PHI1 = FACTOR^{(1.D0 - PHI0(R^{NT}, N)/FACTOR)}
           IF (ILT .EQ. 1) THEN
           TM1 = DNTDZ - N/Z
           TM2 = R*DNTDZ*PHI2(N,R*NT) - N*PHIO(N,R*NT)/Z
           TM3 = DNTDZ*PHI2(R*N,NT) - R*N*PHI0(R*N,NT)/Z
           ELSE
           TM1 = DNTDT
           TM2 = R*DNTDT*PHI2(N,R*NT)
           TM3 = DNTDT*PHI2(R*N,NT)
           END IF
        FDER = (R - 1.DO) * TM1 - TM2/PHI1 + TM3/VAL1
        END IF
      END IF
      RETURN
      END
```

## Pore-diffusion Model Simulator

```
IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*60 TITLE
      CHARACTER*35 XTIT, YTIT
      REAL*8 MUF
      DIMENSION U(15), DIF1(15), DIF2(15), DIF3(15), ROOT(15), VEC1(15),
     &VEC2(15),UPS(15),OBAR(15),CJ0(15),BMAT(15,15),BMATS(15,15)
      REAL*4 TMOD(502),CMOD(502),TEXP(202),CEXP(202),ACTIM,VCOLE,CE,
     &ALFAE1,ETA1,PHI1,GAMMA1
      COMMON /SUMTRM/TERM(15,15),AN1(15),GAMMA,ALFAE,PHI,UTEMP,NCOL1
                                                        ١.
      DATA XTIT, YTIT/
                                UNITLESS TIME
     &' UNITLESS BED-EXIT CONCENTRATION '/
С
С
С
                                     NOVEMBER 12, 1985
       PROGRAMMER: WAYNE BOLDEN
С
С
      THIS PROGRAM CALCULATES THE LIQUID, EFFLUENT-BED, DIMENSIONLESS
С
      CONCENTRATION FOR A LIGAND EXCHANGE COLUMN. IT ASSUMES THAT THE
С
      METAL-RESIN HAS A POROUS MICROSTRUCTURE. LANGMUIR EQUILIBRIUM
С
      EXISTS BETWEEN THE SOLID AND LIQUID PHASES AT EACH POINT IN THE
С
      PORE. TRANSPORT IS GOVERNED BY DIFFUSION OF THE LIGAND IN THE
      PORE FLUID.
С
                  THE EFFLUENT-BED CONCENTRATION CAN BE CALCULATED FOR
С
      LIGAND SORPTION OR ELUTION RUN CONDITIONS. FOR COLUMN REGENERA-
С
      TION, IT HAS BEEN ASSUMED THAT THE BED IS INITIALLY SATURATED
¢
      (OR VERY NEARLY SO) WITH THE LIGAND OF INTEREST. THE MODEL
С
      EQUATIONS (DESCRIBED IN DETAIL ELSEWHERE) ARE SOLVED NUMERICALLY
С
      USING THE METHOD OF ORTHOGONAL COLLOCATION. THE RELEVANT EQUA-
С
      TIONS AND EXPLANATIONS ARE FOUND IN THE FOLLOWING SOURCES:
C
С
      1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL
С
         EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL,
С
         ENGLEWOODS CLIFFS, NJ (1978).
С
С
      2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22,
С
         1483 (1967).
С
С
     3) RAGHAVAN, N.S. AND RUTHVEN, D.M., 'AICHE J,' VOL.29, NO. 6,
С
        922 (1983).
С
С
     4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.33,
С
        593 (1978).
С
С
      5) KATAOKA, T., YOSHIDA, H. AND K. UEYAMA, 'J. CHEM. ENG. JAPAN,'
С
        VOL.5, NO.2, 132 (1972).
С
С
     6) WILSON, E.J. AND C.J. GEANKOPLIS, 'I & E C FUND.,' VOL.5, NO.1,
С
        9, (1966).
```

С C----THE NECESSARY INPUT DATA ARE:-----С С TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С С ---SOLUTION PROPERTIES---С С MUF - FLUID VISCOSITY, CP С RHOF - FLUID-PHASE DENSITY, G/CM\*\*3 DF С - FLUID-PHASE DIFFUSIVITY, CM\*\*2/SEC С С ---SORBENT PROPERTIES---С С - EQUILIBRIUM FACTOR, UNITLESS ALFAE С - REFERENCE SORBENT CONCENTRATION, MG/G RESIN QREF С BETAP - SORBENT POROSITY, CM\*\*3 PORE/CM\*\*3 PARTICLE С RHOP - APPARENT SOLID SORBENT DENSITY (IN UNTREATED H+ FORM). С G/CM\*\*3 PARTICLE - EFFECTIVE PARTICLE-PHASE DIFFUSIVITY OF LIGAND, С DP С CM\*\*2/SEC С D - DIAMETER OF SOLID PARTICLES, CM С С ---FIXED BED PROPERTIES---С С - FRACTIONAL VOIDAGE IN BED, CM\*\*3 VOID/CM\*\*3 BED BETA С DB - BED DIAMETER, CM С ----RUN PARAMETERS---С С С TEMP - COLUMN TEMPERATURE, C - FEED CONCENTRATION FOR LIGAND SORPTION, MG/CM\*\*3 С C0 С (BED VOID CONCENTRATION FOR LIGAND ELUTION) C Q0 - INITIAL SORBENT CONCENTRATION OF BED, MG/G RESIN С Z - BED LENGTH, CM С - VOLUMETRIC FLOW RATE, CM\*\*3/SEC QRATE С - NUMBER DESCRIBING CORRELATION FOR FILM TRANSFER IFTC С COEFFICIENT С = 1 KATAOKA ET AL. J-FACTOR CORRELATION С = 2 WILSON ET AL. J-FACTOR CORRELATION С FTCA - FILM TRANSFER ADJUSTMENT FACTOR С ILR - NUMBER DESCRIBING RUN OPTION С = 1 LIGAND SORPTION (COLUMN LOADING) С = -1 LIGAND ELUTION (COLUMN REGENERATION) С NEXP - NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) С TEXP - VOLUMETRIC THROUGHPUT, CM\*\*3 С (MUST BE GREATER THAN THE BED VOIDAGE VOLUME) С CEXP - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 C С ---NUMERICAL PARAMETERS---С С NCOL1 - NUMBER OF RADIAL INTERIOR COLLOCATION POINTS

C			(MAXIMUM OF 15)	
Ç	NCOL2	-	NUMBER OF AXIAL INTERIOR COLLOCATION POINTS	
С			(MAXIMUM OF 15)	
С	TSTEP	-	SIZE OF DIMENSIONLESS TIME STEP IN NUMERICAL	
С			INTEGRATION	
С	NINSD	-	NUMBER OF INTERNALLY CALCULATED ITERATION SEQUENCES	
С			PER WRITTEN OUTPUT	
С	NWRITE	-	NUMBER OF TIMES THE CALCULATED VALUES ARE WRITTEN	
С			(MAXIMUM OF 500)	
С	FBT	-	FRACTION OF FEED CONCENTRATION NEEDED TO DENOTE	
¢			THE END OF THE RUN (LESS THAN 1)	
С				
C	THE CAL	CUL	ATED VALUES ARE:	
С				
¢	GAMMA ·	-	CAPACITY RATIO (PORE TO SURFACE), UNITLESS	
С				
С	VE	-	SUPERFICIAL FLUID VELOCITY, CM/SEC	
С				
C	RESTIM	-	BED RESIDENCE TIME, SEC	
C				
C	ETA	-	DIMENSIONLESS BED LENGTH PARAMETER	
C				
C	н	-	FLUID-PHASE MASS TRANSFER COEFFICIENT, CM/SEC	
C	<b>5</b> 3777		DINEVETONIECC FILM DECICANNOE DADAWERED	
C a	PHI	-	DIMENSIONLESS FILM RESISTANCE PARAMETER	
0	XX1 ( T )			
C C	MAT(2)	-	CONDIENT AT DIFFERENTIATION WEIGHTS FOR SPHERICAL	
ĉ			GRADIENI AI FARIICEE SORFACE	
č	TEPM(T T)	_	IACDANGIAN DIFFEDENTIATION WEIGHTS FOD SCHEDICAL	
č	10.01(1,0)		LAPLACIAN EVALUATED AT ROOT I	
č				
č	BMATS(I.J)	-	LAGRANGIAN DIFFERENTIATION WEIGHTS FOR AXIAL	
č	(-,-,		GRADIENT EVALUATED AT ROOT I	
č				
c	TF	-	DIMENSIONLESS TIME	
Ċ				
C	TVAL	-	REAL TIME VALUE, SEC	
с			·	
С	VCOLM	-	MODEL-PREDICTED VOLUMETRIC THROUGHPUT, CM**3	
С				
С	QBAR(J)	-	DIMENSIONLESS PARTICLE-AVERAGE SORBENT CONCENTRATION	
С			AT EACH BED-COLLOCATION POSITION	
С				
С	U(NSOL)	-	DIMENSIONLESS EFFLUENT-BED CONCENTRATION	
С	-			
С	QBRBR	-	DIMENSIONLESS BED-AVERAGE (PARTICLE-AVERAGE) SORBENT	
С			CONCENTRATION	
C*************************************				
С				
С	READ THE	T	ITLE OF THE SYSTEM TO BE STUDIED.	
С				

.

```
READ (5,111) TITLE
  111 FORMAT (A60)
С
С
      READ THE SOLUTION PROPERTIES.
С
      READ (5,*) MUF, RHOF, DF
С
С
      READ THE SOLID SORBENT PROPERTIES.
Ċ
      READ (5,*) ALFAE, QREF, BETAP, RHOP, DP, D
С
      READ THE FIXED BED PROPERTIES.
С
Ċ
      READ (5,*) BETA, DB
С
C
      READ THE RUN PARAMETERS. THEN, CALCULATE THE SUPERFICIAL
С
      VELOCITY, THE BED RESIDENCE TIME, THE BED LENGTH PARAMETER
C
      AND NON-DIMENSIONLIZE THE BED SORBENT CONCENTRATION.
С
      ALSO, CALCULATE THE CAPACITY RATIO.
С
      READ (5,*) TEMP, CO, QO, Z, QRATE, IFTC, FTCA, ILR, NEXP
      VE = QRATE/(7.853981634D-01*DB**2)
      RESTIM = Z*BETA/VE
      ETA = 12.*(1. - BETA)*Z*BETAP*DP/(VE*D**2)
      Q0 = Q0/QREF
      GAMMA = BETAP*CO/(RHOP*QREF)
С
С
      READ THE NUMERICAL PARAMETERS.
С
      READ (5,*) NCOL1, NCOL2, TSTEP, NINSD, NWRITE, FBT
С
С
      WRITE THE HEADING.
C
      WRITE (6,201)
  201 FORMAT(1H1,3X, 'NUMERICAL SIMULATION OF A LIGAND EXCHANGE COLUMN'/,
     116X, 'BY ORTHOGONAL COLLOCATION', /, 19X, 'PORE DIFFUSION MODEL')
      WRITE (6,202) TITLE
  202 FORMAT(///,1X,A60)
С
С
      WRITE THE INPUT DATA (AS A CHECK).
С
      WRITE (6,205)
  205 FORMAT(///, 3X, 'THE INPUT DATA ARE AS FOLLOWS:'//)
      WRITE (6,206) MUF
 206 FORMAT(/' THE FLUID-PHASE VISCOSITY IS ',1PD12.5,' CP')
      WRITE (6,207) RHOF
  207 FORMAT(/' THE FLUID-PHASE DENSITY IS ',1PD12.5,' G/CM**3')
      WRITE (6,208) DF
  208 FORMAT(/' THE FLUID-PHASE DIFFUSIVITY IS ',1PD12.5,' CM**2/SEC')
      WRITE(6,209) ALFAE
  209 FORMAT(/,' THE LANGMUIR-TYPE EQUILIBRIUM CONSTANT IS ',1PD12.5)
      WRITE(6,210) QREF
```

```
210 FORMAT(/' THE REFERENCE SORBENT CONCENTRATION IS ', 1PD12.5,
    1' MG/G RESIN')
     WRITE(6,211) BETAP
 211 FORMAT(/' THE SORBENT POROSITY IS ',1PD12.5,' CM**3 PORE/CM**3 PA
    1RTICLE')
     WRITE (6,212) RHOP
 212 FORMAT(/' THE APPARENT SORBENT DENSITY IS ',1PD12.5,' G/CM**3')
     WRITE(6,213) DP
 213 FORMAT(/' THE EFFECTIVE PARTICLE-PHASE DIFFUSIVITY IS ',1PD12.5,
    1' CM**2/SEC')
     WRITE(6,214) D
 214 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ',1PD12.5,' CM')
     WRITE(6,215) BETA
 215 FORMAT(/' THE FRACTIONAL BED VOIDAGE IS ',1PD12.5,' CM**3 VOID/CM
    1**3 BED')
     WRITE (6,216) DB
 216 FORMAT(/' THE BED DIAMETER IS ',1PD12.5,' CM')
     WRITE(6,217) TEMP
 217 FORMAT(/' THE COLUMN TEMPERATURE IS ',1PD10.3,' C')
     WRITE(6,218) CO
 218 FORMAT(/' THE FEED CONCENTRATION FOR LIGAND SORPTION IS ', 1PD12.5
    1,' MG/CM**3')
    WRITE (6,219) 00
 219 FORMAT(/' THE INITIAL BED SORBENT CONCENTRATION IS ', 1PD12.5
    1,' MG/G RESIN')
     WRITE (6,220) Z
 220 FORMAT(/' THE BED LENGTH IS ',1PD12.5,' CM')
     WRITE (6,221) QRATE
 221 FORMAT(/' THE VOLUMETRIC FLOW RATE IS ',1PD12.5,' CM**3/SEC')
     IF (IFTC .EQ. 1) THEN
     WRITE (6,222)
 222 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS DETERMINED FROM THE KA
    1TAOKA ET AL. CORRELATION')
    ELSE
    WRITE (6,223)
223 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS DETERMINED FROM THE WI
    1LSON ET AL. CORRELATION')
    END IF
    WRITE (6,2222) FTCA
2222 FORMAT(/' THE FILM TRANSFER ADJUSTMENT FACTOR IS ',1PD9.2)
     IF (ILR .EQ. 1) THEN
    WRITE (6,224)
224 FORMAT(//'
                THE COLUMN WAS RUN UNDER LOADING CONDITIONS')
    ELSE
    WRITE (6,225)
225 FORMAT(//'
                 THE COLUMN WAS RUN UNDER REGENERATION CONDITIONS')
    END IF
    WRITE (6,226) NCOL1
226 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS',
    1I3)
    WRITE (6,227) NCOL2
227 FORMAT(/' THE NUMBER OF AXIAL INTERIOR COLLOCATION POINTS IS',
```

```
1I3)
      WRITE (6,228) TSTEP
  228 FORMAT(/' THE DIMENSIONLESS TIME STEP IS ', 1PD10.3)
      WRITE (6,229) NINSD
  229 FORMAT(/' THE NUMBER OF INTERNALLY GENERATED ITERATION SEQUENCES
     1IS',I4)
      WRITE (6,230) NWRITE
  230 FORMAT(/' THE NUMBER OF OUTPUT CALCULATED VALUES IS', I4)
С
С
      WRITE OUT THE COLUMN HEADING FOR THE EXPERIMENTAL DATA.
C
      WRITE (6,203)
  203 FORMAT(///,' THE EXPERIMENTAL DATA ARE:',//,6X,'TIME',8X,
     1'VOLUMETRIC',4X,'DIMENSIONLESS',2X,'DIMENSIONLESS',2X,
     2'EXPERIMENTAL',/,18X,'THROUGHPUT',9X,'TIME',6X,'CONCENTRATION',2X,
     3'CONCENTRATION',/,7X,'SEC',11X,'CM**3',39X,'MG/CM**3')
С
      READ THE EXPERIMENTAL DATA, NON-DIMENSIONLIZE IT AND WRITE IT.
С
С
      DO 200 L=1,NEXP
      READ (5,*) VCOLE, CE
      ACTIM = VCOLE/ORATE
      TAU = ACTIM - RESTIM
      TEXP(L) = 4.*TAU*DP/D**2
      CEXP(L) = CE/CO
      WRITE (6,204) ACTIM, VCOLE, TEXP(L), CEXP(L), CE
  204 FORMAT(/,2X,1PE12.5,3X,1PE12.5,3X,2(1PE12.5,3X),1PE12.5)
  200 CONTINUE
C
      CALCULATE THE FILM TRANSFER COEFFICIENT AND THE FILM
С
С
      RESISTANCE PARAMETER.
С
      HINIT = FILMT(MUF, RHOF, VE, BETA, D, DF, IFTC)
      H = FTCA*HINIT
      PHI = H*D/(2.*BETAP*DP)
С
      BEGIN WRITING THE OUTPUT DATA. WRITE THE SUPERFICIAL VELOCITY.
С
С
      THE BED RESIDENCE TIME, THE FILM TRANSFER COEFFICIENT, THE BED
      LENGTH PARAMETER, AND THE FILM RESISTANCE PARAMETER.
С
С
      WRITE (6,231) VE
  231 FORMAT(//,3X,'THE CALCULATED VALUES ARE:',///,' THE SUPERFICIAL V
     1ELOCITY IS ',1PD12.5,' CM/SEC')
      WRITE (6,232) RESTIM
  232 FORMAT(/,' THE BED RESIDENCE TIME IS ',1PD12.5,' SEC')
      WRITE (6,233) GAMMA
  233 FORMAT(/,' THE CAPACITY RATIO IS ', 1PD12.5)
      WRITE (6,234) RESTIM
  234 FORMAT(/.' THE BED RESIDENCE TIME IS '. 1PD12.5.' SEC')
      WRITE (6,235) ETA
  235 FORMAT(/,' THE BED LENGTH PARAMETER IS ',1PD12.5)
```

```
WRITE (6,236) HINIT
```

```
236 FORMAT(/,' THE FILM TRANSFER COEFFICIENT CALCULATED FROM THE',/,
     1' STATED CORRELATION IS ',1PD12.5,' CM/SEC')
      WRITE (6,2366) H
 2366 FORMAT(/,' THE ACTUAL FILM TRANSFER COEFFICIENT IS ',1PD12.5,
     1' CM/SEC')
      WRITE (6,237) PHI
  237 FORMAT(/,' THE FILM RESISTANCE PARAMETER IS ',1PD12.5)
      WRITE(6,238)
  238 FORMAT(/, ' THE COLLOCATION RADIAL COORDINATES ARE: ',/)
      N01 = 0
      N11 = 1
      NT1 = NCOL1 + NO1 + N11
      AL1 = 1.
      BE1 = 0.5
      CALL JCOBI (15, NCOL1, NO1, N11, AL1, BE1, DIF1, DIF2, DIF3, ROOT)
C
С
      WRITE OUT THE RADIAL COLLOCATION POINTS.
С
      DO 1 I = 1,NT1
      R = DSQRT(ROOT(I))
      WRITE(6,240) I,R
  240 FORMAT(1X, 'R(', I2, ') = ', 1PD12.5)
      CALL DFOPR(15,NCOL1,N01,N11,I,1,DIF1,DIF2,DIF3,ROOT,VEC1)
      CALL DFOPR(15,NCOL1,N01,N11,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
         DO 2 J = 1.NT1
C
С
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
      SPHERICAL LAPLACIAN. NOTE THAT
С
         A(I,J) = VEC1(J)
С
         B(I,J) = VEC2(J)
С
         IF (I .EQ. NT1) AN1(J) = VEC1(J)
         TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
    2
         CONTINUE
    1 CONTINUE
      N02 = 1
      N12 = 1
      NT2 = NCOL2 + NO2 + N12
      NSOL = NCOL2 + 1
      AL2 = 0.
      BE2 = 0.
      CALL JCOBI (15, NCOL2, NO2, N12, AL2, BE2, DIF1, DIF2, DIF3, ROOT)
C
С
      SET UP THE FLUID-PHASE CONCENTRATION AT THE PARTICLE SURFACE.
C
      UPO = QO/(ALFAE - (ALFAE - 1.)*QO)
      IF (ILR .EQ. 1) THEN
С
С
      LOADING INITIAL CONDITIONS (SORBENT IS USUALLY FRESH)
С
      U0 = 1.
      ELSE
```

REGENERATION INITIAL CONDITIONS (SORBENT PORE IS LESS THAN 100% SATURATED)

```
C
С
      SATURATED)
С
      UO = 0.
      END IF
      DO 12 J = 2,NT2
      JPARM = J - 1
      CALL DFOPR(15,NCOL2,N02,N12,J,1,DIF1,DIF2,DIF3,ROOT,VEC1)
         DO 13 M = 1, NSOL
С
C
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
      AXIAL GRADIENT IN THE BED CONCENTRATIONS.
С
         BMATS(JPARM, M) = VEC1(M+1)
           IF (JPARM .EQ. M) THEN
           BMATS(M,M) = BMATS(M,M) + ETA*PHI
           END IF
   13
         CONTINUE
      CJO(JPARM) = VEC1(1)
С
С
      INITIALIZE THE BED CONCENTRATIONS.
C .
      ARG = -ETA*PHI*ROOT(J)
         IF (ARG .LT. -23.) THEN
         U(JPARM) = UP0
         ELSE
         U(JPARM) = UPO + (UO - UPO)*DEXP(ARG)
         END IF
   12 CONTINUE
С
C
      THE PARAMETERS FOR THE AXIAL AVERAGING OF THE MEAN PARTICLE
С
      SORBENT CONCENTRATION ARE SET HERE. FIRST, THE ZEROS AND THE
С
      DIFFERENTIATION WEIGHTS OF THE APPROPRIATE JACOBI POLYNOMIAL
С
      ARE CALCULATED.
C
      N00 = 0
      ALQ = 1.
      CALL JCOBI(15,NCOL2,NOQ,N12,ALQ,BE2,DIF1,DIF2,DIF3,VEC1)
C
С
      NEXT, THE OUADRATURE WEIGHTS ARE DETERMINED AND STORED IN THE
Ç
      THE VEC2 ARRAY.
С
      CALL RADAU(15,NCOL2,NOQ,N12,1,AL2,BE2,VEC1,DIF1,VEC2)
С
С
      WRITE OUT THE AXIAL COLLOCATION POINTS AND THE INTEGRATION WEIGHTS
С
      WRITE(6,241)
  241 FORMAT(/, ' THE COLLOCATION AXIAL COORDINATES AND INTEGRATION WEIGH
     1TS ARE:',/)
     DUMVEC = 0.
      IVAL = 1
```

С

```
WRITE(6,242) IVAL, ROOT(IVAL), IVAL, DUMVEC
  242 FORMAT(1X, 'X(',I2,') = ',1PD12.5,' ; W(',I2,') = ',1PD12.5)
      DO 10 I = 2,NT2
      WRITE(6,242) I,ROOT(I),I,VEC2(I-1)
   10 CONTINUE
С
С
      WRITE OUT THE COLUMN HEADING FOR REMAINING THE OUTPUT VARIABLES.
C
      WRITE (6,243)
  243 FORMAT(///,'
                      THE MODEL VALUES ARE: ',//, 2X, 'NUMBER OF', 7X, 'TIME'
     1,8X, 'VOLUMETRIC',4X, 'DIMENSIONLESS',2X, 'DIMENSIONLESS',6X,
     2'MODEL',/,1X,'INTEGRATIONS',17X,'THROUGHPUT',8X,'TIME'
     3,7X, 'CONCENTRATION',2X, 'CONCENTRATION',/,19X, 'SEC',11X, 'CM**3',
     439X,'MG/CM**3')
С
С
      DEFINE THE NUMERICAL INTEGRATION PARAMETERS.
C
      TI = 0.0
      TF = TSTEP
      NEO = NT1
      IWRITE = 0
      DO 3 I = 1, NWRITE
         DO 4 J = 1,NINSD
С
С
      SUBROUTINE "TIMED2" DETERMINES THE INHERENT TIME DEPENDENCY
С
      OF THE AXIAL BED-CONCENTRATION PROFILE BY SOLVING THE SORBENT-
С
      PHASE MATERIAL BALANCE.
С
         CALL TIMED2(TI, TF, Q0, UP0, U, NSOL, NEQ, UPS, QBAR, IFLG)
         IF (IFLG .LT. 0) GO TO 8
             DO 5 M = 1,NSOL
                DO 50 N = 1.NSOL
                BMAT(M,N) = BMATS(M,N)
   50
                CONTINUE
             BMAT(M,NT2) = -CJO(M)*U0 + ETA*PHI*UPS(M)
    5
             CONTINUE
С
С
      AFTER SETTING UP THE APPROPRIATE MATRIX, THE LIOUID-PHASE
С
      MATERIAL BALANCE IS SOLVED BY GAUSSIAN ELIMINATION.
Ċ
         CALL GAUSL(15,15,NSOL,1,BMAT)
             DO 6 M = 1,NSOL
             UTMP = BMAT(M, NT2)
             IF (UTMP .LE. 1.D-04) THEN
             U(M) = 0.D0
             ELSE
             U(M) = UTMP
             END IF
    6
             CONTINUE
         IF (J .LT. NINSD) TF = TF + TSTEP
              IF (ILR .EQ. 1) THEN
```

```
IF (U(NSOL) .GT. FBT) GO TO 30
```
```
ELSE
              IF (I .GT. 20 .AND. U(NSOL) .LT. FBT) GO TO 30
              END IF
    4
         CONTINUE
      NSTEP = I*NINSD
      TVAL = TF*D**2/(4.*DP) + RESTIM
      VCOLM = TVAL*ORATE
      TMOD(I) = TF
      CMOD(I) = U(NSOL)
      CN = U(NSOL)*CO
С
С
      THE RESULTS OF THE CALCULATIONS ARE WRITTEN OUT.
С
      WRITE (6,244) NSTEP, TVAL, VCOLM, TMOD(1), CMOD(1), CN
  244 FORMAT(/,3X,16,5X,1PD12.5,3X,1PD12.5,3X,2(1PD12.5,3X),1PD12.5)
С
      WRITE (6,245)
C 245 FORMAT(1X, ' THE SOLUTION AT THE INTERIOR AXIAL COLLOCATION POINTS
     &IS ')
С
      WRITE (6,246) (L,U(L),L,QBAR(L),L=1,NCOL2)
С
C 246 FORMAT(3X, 'U(',I2,') = ',1PD12.5,'; OBAR(',I2,') = ',1PD12.5)
      TF = TF + TSTEP
      IWRITE = IWRITE + 1
    3 CONTINUE
С
      THE RESULTING PARTICLE-AVERAGE SORBENT CONCENTRATIONS AT EACH
C
С
      BED-COLLOCATION POSITION ARE WRITTEN OUT ALONG WITH THE BED-
C
      AVERAGE SORBENT CONCENTRATION.
C
   30 WRITE(6,31)
   31 FORMAT(/, ' THE PARTICLE-AVERAGE SORBENT CONCENTRATIONS AT THE INTE
     &RIOR COLLOCATION POSITIONS AND THE BED EFFLUENT ARE :')
      QBRBR = 0.
      DO 32 I = 1.NSOL
      QBRBR = QBRBR + VEC2(I)*QBAR(I)
      IPARM = I + 1
      WRITE(6,33) IPARM, QBAR(I)
   33 FORMAT(1X, ' QBAR(', I2, ') = ', 1PD12.5)
   32 CONTINUE
      WRITE(6,34) OBRBR
   34 FORMAT(/,' THE DIMENSIONLESS BED-AVERAGE SORBENT CONCENTRATION IS
     1'.1PD12.5)
      GO TO 22
    8 WRITE (6,9) IFLG, NSTEP, TVAL, VCOLM, TMOD(I), CMOD(I), CN
    9 FORMAT(//,6X,'ERROR HALT... ISTATE = ',I2,/,6X,'THE LAST COMPUTED
     1 VALUES WERE',/,3X,16,5X,1PD12.5,3X,1PD12.5,3X,2(1PD12.5,3X),
     21PD12.5)
      STOP
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
С
      SAME GRAPH.
C
   22 CONTINUE
```

ALFAE1 = ALFAEGAMMA1 = GAMMA ETA1 = ETAPHI1 = PHICALL GRAF (NEXP, IWRITE, TEXP, TMOD, CEXP, CMOD, ALFAE1, GAMMA1, ETA1, &PHI1, TITLE, XTIT, YTIT, ILR) STOP END С FUNCTION FILMT (MUF, RHOF, VE, BETA, D, DF, IFTC) IMPLICIT REAL\*8 (A-H,O-Z) DOUBLE PRECISION MUF C----С С THIS SUBPROGRAM CALCULATES THE FILM TRANSFER COEFFICIENT С FROM THE SHERWOOD CORRELATION OR THE ONDA EQUATION (DEPENDING C ON THE VALUE OF IFTC). С C---\_\_\_\_\_ С SC = MUF\*1.D-02/(RHOF\*DF)RE = D\*VE\*RHOF/(MUF\*1.D-02)IF (IFTC .EQ. 1) THEN С С THE FILM TRANSFER COEFFICIENT IS CALCULATED ACCORDING TO THE С KATAOKA ET AL. J-FACTOR CORRELATION. С RE = RE/(1. - BETA)FILMT = 1.85\*VE\*(BETA/(1. - BETA))\*\*(1./3.)/BETA\* &((RE\*SC)\*\*(-2./3.)) ELSE С C THE FILM TRANSFER COEFFICIENT IS CALCULATED ACCORDING TO THE Ç WILSON ET AL. ANALOGY. С FILMT = 1.09\*VE/BETA\*((RE\*SC)\*\*(-2./3.)) END IF RETURN END С SUBROUTINE TIMED2(TI0, TF0, Q0, UP0, U, NSOL, NEQ, UPS, QBAR, ISTATE) IMPLICIT REAL\*8 (A-H,O-Z) EXTERNAL FN2 DIMENSION U(1), UPS(1), OBAR(1), UPARR(15, 15), UPVAL(15), RWORK(260), 1IWORK(20)COMMON /SUMTRM/TERM(15,15),AN1(15),GAMMA,ALFAE,PHI,UTEMP,NCOL1 С С THIS SUBROUTINE SOLVES THE TRANSIENT, SPHERICAL DIFFUSION С PROBLEM (WITH FILM TRANSFER) AT EACH AXIAL COLLOCATION POINT. С IT DETERMINES THE INHERENT TIME DEPENDENCY OF THE AXIAL BED-C CONCENTRATION PROFILE.

С C-\_\_\_\_\_\_ . С DO 1 J = 1,NSOL TI = TIOTF = TF0UTEMP = U(J)IF (TIO .EQ. O.) THEN DO 2 M = 1, NCOL1UPVAL(M) = UPOCONTINUE 2 UPVAL(NEQ) = QOELSE DO 3 M = 1, NEQUPVAL(M) = UPARR(J,M)3 CONTINUE END IF IF (DABS(UTEMP - UPO) .GT. 1.D-04) THEN С С IF THERE IS A SIGNIFICANT DRIVING FORCE FOR TRANSFER OF THE С LIGAND, THEN THE SPHERICAL DIFFUSION PROBLEM IS SOLVED AT ¢ THAT AXIAL-COLLOCATION POSITION. С ITOL = 1ATOL = 1.D-04RTOL = 1.D-04ITASK = 1IOPT = 0ISTATE = 1LRW = 260LIW = 20ML = 0MU = 0MF = 10CALL LSODE (FN2, NEQ, UPVAL, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT, &RWORK, LRW, IWORK, LIW, JAC, MF) IF (ISTATE .LT. 0) RETURN USUM = 0.DO 4 M = 1,NCOL1 UPARR(J,M) = UPVAL(M)USUM = USUM + AN1(M)\*UPVAL(M)4 CONTINUE UPARR(J, NEQ) = UPVAL(NEQ)QBAR(J) = UPVAL(NEQ)UPS(J) = PHI\*(UTEMP - 2.\*USUM/PHI)/(PHI + 2.\*AN1(NEQ))ELSE С С OTHERWISE, THE INITIAL CONDITIONS ARE REINSTATED. С UPS(J) = UPODO 5 M = 1, NCOL1 UPARR(J,M) = UPO

```
5
       CONTINUE
  UPARR(J, NEQ) = QO
  QBAR(J) = QO
  END IF
1 CONTINUE
  TIO = TFO
  RETURN
  END
  SUBROUTINE FN2(NEQ,X,Y,DY)
  THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
  SUBROUTINE LSODE.
  IMPLICIT REAL*8 (A-H,O-Z)
  DIMENSION Y(NEQ), DY(NEQ)
  COMMON /SUMTRM/TM(15,15), AN1(15), GAMMA, ALFAE, PHI, UVAL, NCOL1
  FP(T) = ALFAE/(1. + (ALFAE - 1.)*T)**2
  DENOM(T) = 1. + FP(T)/GAMMA
  SUM2 = 0.
  RECALL, NEQ = NT1 = NCOL1 + 1.
  DO 1 I = 1,NCOL1
  TEMPY = Y(I)
  SUM1 = 0.
    DO 2 J = 1,NCOL1
    SUM1 = SUM1 + (TM(I,J) - 2.*TM(I,NEQ)*AN1(J)/(2.*AN1(NEQ) +
           PHI))*Y(J)
 &
2
    CONTINUE
  SUM1 = SUM1 + TM(I, NEQ) * PHI * UVAL/(2.*AN1(NEQ) + PHI)
  DY(I) = SUM1/DENOM(TEMPY)
  SUM2 = SUM2 + AN1(I) * TEMPY
1 CONTINUE
  DY(NEQ) = 6.*GAMMA*PHI*(SUM2 + AN1(NEQ)*UVAL)/(2.*AN1(NEQ) + PHI)
  RETURN
```

C

C C

C

С

C C

С

END

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#### Solid-diffusion\_Model\_Simulator

```
IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*60 TITLE
      CHARACTER*35 XTIT, YTIT
      REAL*8 MUF
      DIMENSION U(15), DIF1(15), DIF2(15), DIF3(15), ROOT(15), VEC1(15),
     &VEC2(15), US(15), QBAR(15), CJO(15), BMAT(15,15), BMATS(15,15)
      REAL*4 TMOD(502),CMOD(502),TEXP(202),CEXP(202),ACTIM,VCOLE,CE,
     &ALFAE1,ETA1,PHI1
      COMMON /SUMTRM/TERM(15,15), AN1(15), UVAL, PHI, PSI, ALFAE, NT1, NCOL1
      DATA XTIT, YTIT/'
                                UNITLESS TIME
     &' UNITLESS BED-EXIT CONCENTRATION '/
С
С
C
       PROGRAMMER: WAYNE BOLDEN
                                     NOVEMBER 12, 1985
С
C
      THIS PROGRAM CALCULATES THE LIQUID, EFFLUENT-BED, DIMENSIONLESS
С
      CONCENTRATION FOR A LIGAND EXCHANGE COLUMN. IT ASSUMES THE
С
      METAL-RESIN TO BE A PSEUDO-HOMOGENEOUS SOLID. LANGMUIR EQUILI-
С
      BRIUM OCCURS AT THE LIQUID-SOLID INTERFACE. SOLID DIFFUSION
С
      THROUGH THE SORBENT PARTICLES GOVERNS THE TRANSPORT MECHANISM.
      THE EFFLUENT-BED CONCENTRATION CAN BE CALCULATED FOR LIGAND
C
С
      SORPTION OR ELUTION RUN CONDITIONS. FOR COLUMN REGENERATION,
С
      IT HAS BEEN ASSUMED THAT THE BED IS INITIALLY SATURATED (OR VERY
Ç
      NEARLY SO) WITH THE LIGAND OF INTEREST. THE MODEL EQUATIONS
С
      (DESCRIBED IN DETAIL ELSEWHERE) ARE SOLVED NUMERICALLY USING
С
      THE METHOD OF ORTHOGONAL COLLOCATION. THE RELEVANT EQUATIONS
Ċ
      AND EXPLANATIONS ARE FOUND IN THE FOLLOWING SOURCES:
С
      1) VILLADSEN, J AND M.L. MICHELSEN, "SOLUTION OF DIFFERENTIAL
С
С
         EQUATION MODELS BY POLYNOMIAL APPROXIMATION," PRENTICE-HALL,
C
         ENGLEWOODS CLIFFS, NJ (1978).
С
      2) VILLADSEN, J.V. AND W.E. STEWART, 'CHEM. ENG. SCI.,' VOL.22,
С
С
         1483 (1967).
С
С
      3) RAGHAVAN, N.S. AND RUTHVEN, D.M., 'AICHE J,' VOL.29, NO. 6,
С
         922 (1983).
C
С
      4) LIAPIS, A.I. AND D.W.T.RIPPIN, 'CHEM. ENG. SCI.,' VOL.33,
С
         593 (1978).
С
С
      5) KATAOKA, T., YOSHIDA, H. AND K. UEYAMA, 'J. CHEM. ENG. JAPAN,'
¢
         VOL.5, NO.2, 132 (1972).
С
C
     6) WILSON, E.J. AND C.J. GEANKOPLIS, 'I & E C FUND.,' VOL.5, NO.1,
С
         9, (1966).
```

С C----THE NECESSARY INPUT DATA ARE:-----C С TITLE - TITLE OF THE SYSTEM (MAXIMUM OF 60 CHARACTERS) С С С ---SOLUTION PROPERTIES---¢ С MUF - FLUID VISCOSITY, CP Ç - FLUID-PHASE DENSITY, G/CM\*\*3 RHOF С DF FLUID-PHASE DIFFUSIVITY, CM\*\*2/SEC С С ---SOLID SORBENT PROPERTIES---С С ALFAE - EQUILIBRIUM FACTOR, UNITLESS С OREF - REFERENCE SORBENT CONCENTRATION, MG/G RESIN С DP - EFFECTIVE PARTICLE-PHASE DIFFUSIVITY OF LIGAND. С CM\*\*2/SEC C D - DIAMETER OF SOLID PARTICLES, CM С С ---FIXED BED PROPERTIES---С C RHOB - BULK DENSITY OF BED (IN CU++, LIGAND-SWOLLEN FORM), С G/CM\*\*3 BED С - FRACTIONAL VOIDAGE IN BED, CM\*\*3 VOID/CM\*\*3 BED BETA С DB - BED DIAMETER, CM С С ---RUN PARAMETERS---С С TEMP - COLUMN TEMPERATURE, C C C0 - FEED CONCENTRATION FOR LIGAND SORPTION, MG/CM\*\*3 С (BED VOID CONCENTRATION FOR LIGAND ELUTION) С - INITIAL SORBENT CONCENTRATION OF BED, MG/G RESIN Q0 С - BED LENGTH, CM Z С VOLUMETRIC FLOW RATE, CM\*\*3/SEC QRATE -С -NUMBER DESCRIBING CORRELATION FOR FILM TRANSFER IFTC С COEFFICIENT С = 1 KATAOKA ET AL. J-FACTOR CORRELATION C = 2 WILSON ET AL. J-FACTOR CORRELATION С FILM TRANSFER ADJUSTMENT FACTOR FTCA C NUMBER DESCRIBING RUN OPTION ILR С = 1 LIGAND SORPTION (COLUMN LOADING) С = -1 LIGAND ELUTION (COLUMN REGENERATION) С NUMBER OF EXPERIMENTAL DATA PAIRS (MAXIMUM OF 60) NEXP С TEXP VOLUMETRIC THROUGHPUT, CM\*\*3 С (MUST BE GREATER THAN THE BED VOIDAGE VOLUME) - EXPERIMENTAL CONCENTRATION, MG/CM\*\*3 С CEXP С С ---NUMERICAL PARAMETERS---С С PSI - STIFFNESS FACTOR С NCOL1 - NUMBER OF RADIAL INTERIOR COLLOCATION POINTS

Ç			(MAXIMUM OF 14)
С	NCOL2	-	NUMBER OF AXIAL INTERIOR COLLOCATION POINTS
С			(MAXIMUM OF 15)
С	TSTEP	-	SIZE OF DIMENSIONLESS TIME STEP IN NUMERICAL
С			INTEGRATION
С	NINSD	-	NUMBER OF INTERNALLY CALCULATED ITERATION SEQUENCES
С			PER WRITTEN OUTPUT
С	NWRITE	-	NUMBER OF TIMES THE CALCULATED VALUES ARE WRITTEN
С			(MAXIMUM OF 500)
С	FBT	-	FRACTION OF FEED CONCENTRATION NEEDED TO DENOTE
С			THE END OF THE RUN (LESS THAN 1)
С			
C-	THE CAL	CUL	ATED VALUES ARE:
С			
С	VE	-	SUPERFICIAL FLUID VELOCITY, CM/SEC
C			
С	RESTIM	-	BED RESIDENCE TIME, SEC
С			
C	ETA	-	DIMENSIONLESS BED LENGTH PARAMETER
C			
С	Н	-	FLUID-PHASE MASS TRANSFER COEFFICIENT, CM/SEC
С			
С	PHI	-	DIMENSIONLESS FILM RESISTANCE PARAMETER
C			
С	AN1(J)	-	LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL
С			GRADIENT AT PARTICLE SURFACE
Ç			
С	TERM(I,J)	-	LAGRANGIAN DIFFERENTIATION WEIGHTS FOR SPHERICAL
С			LAPLACIAN EVALUATED AT ROOT I
С			
С	BMATS(I,J)	-	LAGRANGIAN DIFFERENTIATION WEIGHTS FOR AXIAL
Ç			GRADIENT EVALUATED AT ROOT I
С			
C	TF	-	DIMENSIONLESS TIME
C			
С	TVAL	-	REAL TIME VALUE, SEC
С			4
С	VCOLM	-	MODEL-PREDICTED VOLUMETRIC THROUGHPUT, CM**3
С			
С	QBAR(J)	-	DIMENSIONLESS PARTICLE-AVERAGE SORBENT CONCENTRATION
С			AT EACH BED-COLLOCATION POSITION
С			
С	U(NSOL)	-	DIMENSIONLESS EFFLUENT-BED CONCENTRATION
С			
Ç	QBRBR	-	DIMENSIONLESS BED-AVERAGE (PARTICLE-AVERAGE) SORBENT
C.			CONCENTRATION
C*	****	(**	***************************************
C			
C	READ THE	5 T.	ITLE OF THE SYSTEM TO BE STUDIED.
C	/-		
	READ (5,	,11	L) TITLE
	111 FORMAT (	(A6(	J)

•

```
С
С
      READ THE SOLUTION PROPERTIES.
С
      READ (5,*) MUF, RHOF, DF
С
С
      READ THE SOLID SORBENT PROPERTIES.
С
      READ (5,*) ALFAE, QREF, DP, D
С
С
      READ THE FIXED BED PROPERTIES.
С
      READ (5,*) RHOB, BETA, DB
С
С
      READ THE RUN PARAMETERS. THEN, CALCULATE THE SUPERFICIAL
С
      VELOCITY, THE BED RESIDENCE TIME, THE BED LENGTH PARAMETER
      AND NON-DIMENSIONALIZE THE BED SORBENT CONCENTRATION.
С
С
      READ (5,*) TEMP, CO, QO, Z, QRATE, IFTC, FTCA, ILR, NEXP
      VE = QRATE/(7.853981634D-01*DB**2)
      RESTIM = Z*BETA/VE
      ETA = 12.*Z*RHOB*DP*OREF/(VE*CO*D**2)
      Q0 = Q0/QREF
С
С
      READ THE NUMERICAL PARAMETERS.
С
      READ (5,*) PSI, NCOL1, NCOL2, TSTEP, NINSD, NWRITE, FBT
Ċ
С
      WRITE THE HEADING.
C
      WRITE (6,201)
  201 FORMAT(1H1, 3X, 'NUMERICAL SIMULATION OF A LIGAND EXCHANGE COLUMN'/,
     116X, 'BY ORTHOGONAL COLLOCATION', /, 18X, 'SOLID DIFFUSION MODEL')
      WRITE (6,202) TITLE
  202 FORMAT(///,1X,A60)
С
С
      WRITE THE INPUT DATA (AS A CHECK).
С
      WRITE (6,205)
  205 FORMAT(///;3X, 'THE INPUT DATA ARE AS FOLLOWS:'//)
      WRITE (6,206) MUF
  206 FORMAT(/' THE FLUID-PHASE VISCOSITY IS ',1PD12.5,' CP')
      WRITE (6,207) RHOF
  207 FORMAT(/' THE FLUID-PHASE DENSITY IS ',1PD12.5,' G/CM**3')
      WRITE (6,208) DF
  208 FORMAT(/' THE FLUID-PHASE DIFFUSIVITY IS ',1PD12.5,' CM**2/SEC')
      WRITE(6,209) ALFAE
  209 FORMAT(/,' THE LANGMUIR-TYPE EQUILIBRIUM CONSTANT IS ',1PD12.5)
     WRITE(6,210) QREF
  210 FORMAT(/' THE REFERENCE SORBENT CONCENTRATION IS ', 1PD12.5,
     1' MG/G RESIN')
     WRITE(6,211) DP
 211 FORMAT(/' THE EFFECTIVE PARTICLE-PHASE DIFFUSIVITY IS ',1PD12.5,
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```
1' CM**2/SEC')
     WRITE(6,212) D
 212 FORMAT(/' THE AVERAGE PARTICLE DIAMETER IS ', 1PD12.5, ' CM')
     WRITE(6,213) RHOB
 213 FORMAT(/' THE BULK BED DENSITY IS ',1PD12.5,' G/CM**3')
     WRITE(6,214) BETA
 214 FORMAT(/' THE FRACTIONAL BED VOIDAGE IS ',1PD12.5,' CM**3 VOID/CM
    1**3 BED')
     WRITE (6,215) DB
 215 FORMAT(/' THE BED DIAMETER IS ',1PD12.5,' CM')
     WRITE(6,216) TEMP
 216 FORMAT(/' THE COLUMN TEMPERATURE IS ',1PD10.3,' C')
     WRITE(6,217) CO
 217 FORMAT(/' THE FEED CONCENTRATION FOR LIGAND SORPTION IS ', 1PD12.5
    1,' MG/CM**3')
    WRITE(6,218) 00
 218 FORMAT(/' THE INITIAL BED SORBENT CONCENTRATION IS ', 1PD12.5
    1,' MG/G RESIN')
    WRITE (6,219) Z
 219 FORMAT(/' THE BED LENGTH IS ',1PD12.5,' CM')
     WRITE (6,220) QRATE
 220 FORMAT(/' THE VOLUMETRIC FLOW RATE IS ',1PD12.5,' CM**3/SEC')
     IF (IFTC .EQ. 1) THEN
     WRITE (6,221)
 221 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS DETERMINED FROM THE KA
    ITAOKA ET AL. CORRELATION')
    ELSE
    WRITE (6,222)
 222 FORMAT(/' THE FILM TRANSFER COEFFICIENT IS DETERMINED FROM THE WI
    1LSON ET AL. CORRELATION')
    END IF
    WRITE (6,2222) FTCA
2222 FORMAT(/' THE FILM TRANSFER ADJUSTMENT FACTOR IS ', 1PD9.2)
    IF (ILR .EQ. 1) THEN
    WRITE (6,223)
                 THE COLUMN WAS RUN UNDER LOADING CONDITIONS')
223 FORMAT(//'
    ELSE
    WRITE (6,224)
224 FORMAT(//'
                 THE COLUMN WAS RUN UNDER REGENERATION CONDITIONS')
    END IF
    WRITE (6,225) PSI
225 FORMAT(/' THE STIFFNESS FACTOR IS ',1PD10.3)
    WRITE (6,226) NCOL1
226 FORMAT(/' THE NUMBER OF RADIAL INTERIOR COLLOCATION POINTS IS',
   113)
    WRITE (6,227) NCOL2
227 FORMAT(/' THE NUMBER OF AXIAL INTERIOR COLLOCATION POINTS IS',
   113)
    WRITE (6,228) TSTEP
228 FORMAT(/' THE DIMENSIONLESS TIME STEP IS ', 1PD10.3)
    WRITE (6,229) NINSD
229 FORMAT(/' THE NUMBER OF INTERNALLY GENERATED ITERATION SEQUENCES
```

283

```
1IS',I4)
      WRITE (6,230) NWRITE
  230 FORMAT(/' THE NUMBER OF OUTPUT CALCULATED VALUES IS', 14)
С
С
      WRITE OUT THE COLUMN HEADING FOR THE EXPERIMENTAL DATA.
С
      WRITE (6,203)
  203 FORMAT(///,'
                     THE EXPERIMENTAL DATA ARE: ',//,6X, 'TIME',8X,
     1'VOLUMETRIC',4X,'DIMENSIONLESS',2X,'DIMENSIONLESS',2X,
     2'EXPERIMENTAL',/,18X,'THROUGHPUT',9X,'TIME',6X,'CONCENTRATION',2X,
     3'CONCENTRATION',/,7X,'SEC',11X,'CM**3',39X,'MG/CM**3')
С
С
      READ THE EXPERIMENTAL DATA, NON-DIMENSIONLIZE IT AND WRITE IT.
С
      DO 200 L=1.NEXP
      READ (5,*) VCOLE,CE
      ACTIM = VCOLE/ORATE
      TAU = ACTIM - RESTIM
      TEXP(L) = 4.*TAU*DP/D**2
      CEXP(L) = CE/CO
      WRITE (6,204) ACTIM, VCOLE, TEXP(L), CEXP(L), CE
  204 FORMAT(/,2X,1PE12.5,3X,1PE12.5,3X,2(1PE12.5,3X),1PE12.5)
  200 CONTINUE
С
С
      CALCULATE THE FILM TRANSFER COEFFICIENT AND THE FILM
С
      RESISTANCE PARAMETER.
С
      HINIT = FILMT(MUF, RHOF, VE, BETA, D, DF, IFTC)
      H = FTCA*HINIT
      PHI = H^{(1. - BETA) CO^{D}/(2.*RHOB^{DP}QREF)
С
С
    BEGIN WRITING THE OUTPUT DATA. WRITE THE SUPERFICIAL VELOCITY,
С
      THE BED RESIDENCE TIME. THE FILM TRANSFER COEFFICIENT. THE BED
С
      LENGTH PARAMETER, AND THE FILM RESISTANCE PARAMETER.
С
      WRITE (6,231) VE
  231 FORMAT(//,3X,'THE CALCULATED VALUES ARE:',///,' THE SUPERFICIAL V
     1ELOCITY IS ',1PD12.5,' CM/SEC')
     WRITE (6,232) RESTIM
  232 FORMAT(/,' THE BED RESIDENCE TIME IS ',1PD12.5,' SEC')
     WRITE (6,233) ETA
  233 FORMAT(/,' THE BED LENGTH PARAMETER IS ',1PD12.5)
     WRITE (6,234) HINIT
  234 FORMAT(/,' THE FILM TRANSFER COEFFICIENT CALCULATED FROM THE',/,
     1' STATED CORRELATION IS ',1PD12.5,' CM/SEC')
     WRITE (6,235) H
  235 FORMAT(/,' THE ACTUAL FILM TRANSFER COEFFICIENT IS ',1PD12.5,
     1' CM/SEC')
     WRITE (6,236) PHI
  236 FORMAT(/,' THE FILM RESISTANCE PARAMETER IS '.1PD12.5)
     WRITE(6,237)
  237 FORMAT(/,' THE COLLOCATION RADIAL COORDINATES ARE: ',/)
```

```
N01 = 0
    N11 = 1
    NT1 = NCOL1 + NO1 + N11
    AL1 = 1.
    BE1 = 0.5
    CALL JCOBI (15, NCOL1, N01, N11, AL1, BE1, DIF1, DIF2, DIF3, ROOT)
    WRITE OUT THE RADIAL COLLOCATION POINTS.
    DO 1 I = 1,NT1
    R = DSQRT(ROOT(I))
    WRITE(6,239) I,R
239 FORMAT(1X, 'R(', I2, ') = ', 1PD12.5)
    CALL DFOPR(15,NCOL1,N01,N11,I,1,DIF1,DIF2,DIF3,ROOT,VEC1)
    CALL DFOPR(15,NCOL1,N01,N11,I,2,DIF1,DIF2,DIF3,ROOT,VEC2)
       DO 2 J = 1,NT1
    CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
    SPHERICAL LAPLACIAN. NOTE THAT
       A(I,J) = VEC1(J)
       B(I,J) = VEC2(J)
       IF (I .EQ. NT1) AN1(J) = VEC1(J)
       TERM(I,J) = 4.*ROOT(I)*VEC2(J) + 6.*VEC1(J)
 2
       CONTINUE
  1 CONTINUE
   N02 = 1
   N12 = 1
   NT2 = NCOL2 + NO2 + N12
   NSOL = NCOL2 + 1
   AL2 = 0.
   BE2 = 0.
   CALL JCOBI (15, NCOL2, NO2, N12, AL2, BE2, DIF1, DIF2, DIF3, ROOT)
   SET THE FLUID-PHASE CONCENTRATION AT THE PARTICLE SURFACE.
   USP = QO/(ALFAE - (ALFAE - 1.)*QO)
    IF (ILR .EQ. 1) THEN
   LOADING INITIAL CONDITIONS (SORBENT IS USUALLY FRESH)
   U0 = 1.
   ELSE
   REGENERATION INITIAL CONDITIONS (SORBENT IS LESS THAN 100%
   SATURATED)
   U0 = 0.
   END IF
   DO 12 J = 2,NT2
   JPARM = J - 1
```

C C

С

C C

С

С

С

С

C C

С

C C

С

C C

С

С

```
CALL DFOPR(15,NCOL2,N02,N12,J,1,DIF1,DIF2,DIF3,ROOT,VEC1)
```

```
DO 13 M = 1,NSOL
C
С
      CALCULATE THE LAGRANGIAN DIFFERENTIATION WEIGHTS FOR THE
С
      AXIAL GRADIENT IN THE BED CONCENTRATIONS.
C
         BMATS(JPARM,M) = VEC1(M+1)
            IF (JPARM .EO. M) THEN
           BMATS(M,M) = BMATS(M,M) + ETA*PHI
           END IF
   13
         CONTINUE
      CJO(JPARM) = VEC1(1)
С
С
      INITIALIZE THE BED CONCENTRATIONS.
С
      ARG = -ETA*PHI*ROOT(J)
         IF (ARG .LT. -23.) THEN
         U(JPARM) = USP
         ELSE
         U(JPARM) = USP + (UO - USP)*DEXP(ARG)
         END IF
   12 CONTINUE
С
С
      THE PARAMETERS FOR THE AXIAL AVERAGING OF THE MEAN PARTICLE
С
      SORBENT CONCENTRATION ARE SET HERE. FIRST, THE ZEROS AND THE
С
      DIFFERENTIATION WEIGHTS OF THE APPROPRIATE JACOBI POLYNOMIAL
С
      ARE CALCULATED.
Ċ
      NOQ = 0
      ALQ = 1.
      CALL JCOBI (15, NCOL2, NOQ, N12, ALQ, BE2, DIF1, DIF2, DIF3, VEC1)
С
С
      NEXT, THE QUADRATURE WEIGHTS ARE DETERMINED AND STORED IN THE
Ċ
      THE VEC2 ARRAY.
С
      CALL RADAU(15,NCOL2,NOQ,N12,1,AL2,BE2,VEC1,DIF1,VEC2)
С
С
      WRITE OUT THE AXIAL COLLOCATION POINTS AND THE INTEGRATION WEIGHTS
С
      WRITE(6, 240)
  240 FORMAT(/, ' THE COLLOCATION AXIAL COORDINATES AND INTEGRATION WEIGH
     1TS ARE:',/)
      DUMVEC = 0.
      IVAL = 1
      WRITE(6,241) IVAL, ROOT(IVAL), IVAL, DUMVEC
  241 FORMAT(1X, 'X(',I2,') = ', 1PD12.5,'; W(',I2,') = ', 1PD12.5)
      DO 10 I = 2,NT2
      WRITE(6,241) I,ROOT(I),I,VEC2(I-1)
   10 CONTINUE
С
С
      WRITE OUT THE COLUMN HEADING FOR REMAINING THE OUTPUT VARIABLES.
С
      WRITE (6,242)
```

```
242 FORMAT(///,' THE MODEL VALUES ARE:',//,2X,'NUMBER OF',7X,'TIME'
     1,8X,'VOLUMETRIC',4X,'DIMENSIONLESS',2X,'DIMENSIONLESS',6X,
     2'MODEL',/,1X,'INTEGRATIONS',17X,'THROUGHPUT',8X,'TIME'
     3,7X, 'CONCENTRATION',2X, 'CONCENTRATION',/,19X, 'SEC',11X, 'CM**3',
     439X,'MG/CM**3')
Ç
С
      DEFINE THE NUMERICAL INTEGRATION PARAMETERS.
С
      TI = 0.0
      TF = TSTEP
      NEQ = NT1 + 1
      IWRITE = 0
      DO 3 I = 1,NWRITE
         DO 4 J = 1,NINSD
С
С
      SUBROUTINE "TIMED1" DETERMINES THE INHERENT TIME DEPENDENCY
      OF THE AXIAL BED-CONCENTRATION PROFILE BY SOLVING THE SORBENT-
С
С
      PHASE MATERIAL BALANCE.
C
         CALL TIMED1(TI, TF, Q0, USP, U, NSOL, NEQ, US, QBAR, IFLG)
         IF (IFLG .LT. 0) GO TO 8
             DO 5 M = 1,NSOL
                DO 50 N = 1,NSOL
                BMAT(M,N) = BMATS(M,N)
   50
                CONTINUE
             BMAT(M,NT2) = -CJO(M)*UO + ETA*PHI*US(M)
    5
             CONTINUE
С
С
      AFTER SETTING UP THE APPROPRIATE MATRIX, THE LIQUID-PHASE
С
      MATERIAL BALANCE IS SOLVED BY GAUSSIAN ELIMINATION.
С
         CALL GAUSL(15,15,NSOL,1,BMAT)
             DO 6 M = 1, NSOL
             UTMP = BMAT(M,NT2)
             IF (UTMP .LE. 1.D-04) THEN
             U(M) = 0.D0
             ELSE
             U(M) = UTMP
             END IF
    6
             CONTINUE
         IF (J .LT. NINSD) TF = TF + TSTEP
              IF (ILR .EQ. 1) THEN
              IF (U(NSOL) .GT. FBT) GO TO 30
              ELSE
              IF (I .GT. 20 .AND. U(NSOL) .LT. FBT) GO TO 30
              END IF
    4
         CONTINUE
      NSTEP = I*NINSD
      TVAL = TF*D**2/(4.*DP) + RESTIM
      VCOLM = TVAL*QRATE
      TMOD(I) = TF
      CMOD(I) = U(NSOL)
```

```
CN = U(NSOL)*CO
C
С
      THE RESULTS OF THE CALCULATIONS ARE WRITTEN OUT.
С
      WRITE (6,243) NSTEP, TVAL, VCOLM, TMOD(I), CMOD(I), CN
  243 FORMAT(/,3X,16,5X,1PD12.5,3X,1PD12.5,3X,2(1PD12.5,3X),1PD12.5)
      WRITE (6,244)
С
C 244 FORMAT(1X.' THE SOLUTION AT THE INTERIOR AXIAL COLLOCATION POINTS
С
     &IS ')
      WRITE (6,245) (L,U(L),L,QBAR(L),L=1,NCOL2)
С
C 245 FORMAT(3X,'U(',I2,') = ',1PD12.5,'; QBAR(',I2,') = ',1PD12.5)
      TF = TF + TSTEP
      IWRITE = IWRITE + 1
    3 CONTINUE
C
С
      THE RESULTING PARTICLE-AVERAGE SORBENT CONCENTRATIONS AT EACH
С
      BED-COLLOCATION POSITION ARE WRITTEN OUT ALONG WITH THE BED-
С
      AVERAGE SORBENT CONCENTRATION.
С
   30 WRITE(6.31)
   31 FORMAT(/,' THE PARTICLE-AVERAGE SORBENT CONCENTRATIONS AT THE INTE
     &RIOR COLLOCATION POSITIONS AND THE BED EFFLUENT ARE :')
      OBRBR = 0.
      DO 32 I = 1,NSOL
      QBRBR = QBRBR + VEC2(I)*QBAR(I)
      IPARM = I + 1
      WRITE(6,33) IPARM, OBAR(I)
   33 FORMAT(1X, ' QBAR(', I2, ') = ', 1PD12.5)
   32 CONTINUE
      WRITE(6,34) QBRBR
   34 FORMAT(/, ' THE DIMENSIONLESS BED-AVERAGE SORBENT CONCENTRATION IS
     1',1PD12.5)
      GO TO 22
    8 WRITE (6,9) IFLG, NSTEP, TVAL, VCOLM, TMOD(I), CMOD(I), CN
    9 FORMAT(//,6X,'ERROR HALT... ISTATE = ',12,/,6X,'THE LAST COMPUTED
     1 VALUES WERE',/,3X,16,5X,1PD12.5,3X,1PD12.5,3X,2(1PD12.5,3X),
     21PD12.5)
      STOP
С
С
      FINALLY, PLOT THE MODEL AND EXPERIMENTAL RESULTS ON THE
С
      SAME GRAPH.
С
   22 CONTINUE -
      ALFAE1 = ALFAE
      ETA1 \approx ETA
      PHI1 = PHI
      CALL GRAF (NEXP, IWRITE, TEXP, TMOD, CEXP, CMOD, ALFAE1, ETA1, PHI1, TITLE,
     &XTIT, YTIT, ILR)
      STOP
      END
С
      SUBROUTINE TIMED1(TI0,TF0,00,USP,U,NSOL,NEO,US,OBAR,ISTATE)
```

```
IMPLICIT REAL*8 (A-H,O-Z)
      EXTERNAL FN1, JN1
      DIMENSION U(1), US(1), QBAR(1), Q(15, 15), QVAL(15), RWORK(382),
     &IWORK(35)
      COMMON /SUMTRM/TERM(15,15),AN1(15),UVAL,PHI,PSI,ALFAE,NT1,NCOL1
C----
         С
С
       THIS SUBROUTINE SOLVES THE TRANSIENT, SPHERICAL DIFFUSION
С
     PROBLEM (WITH FILM TRANSFER) AT EACH AXIAL COLLOCATION POINT.
     IT DETERMINES THE INHERENT TIME DEPENDENCY OF THE AXIAL BED-
С
С
     CONCENTRATION PROFILE.
C
        C-
С
     DO 1 J = 1,NSOL
     TI = TIO
     TF = TFO
     UVAL = U(J)
     IF (TIO .EQ. 0.) THEN
             DO 2 M = 1, NEQ
             QVAL(M) = QO
             CONTINUE
    2
     ELSE
             DO 3 M = 1, NEQ
             QVAL(M) = Q(J,M)
    3
             CONTINUE
     END IF
     IF (DABS(UVAL - USP) .GT. 1.D-04) THEN
С
С
     IF THERE IS A SIGNIFICANT DRIVING FORCE FOR TRANSFER OF THE
     LIGAND, THEN THE SPHERICAL DIFFUSION PROBLEM IS SOLVED AT
С
     THAT AXIAL-COLLOCATION POSITION.
С
С
     ITOL = 1
     ATOL = 1.D-04
     RTOL = 1.D-04
     ITASK = 1
     IOPT = 0
     ISTATE = 1
     LRW = 382
     LIW = 35
     ML = 0
     MU = 0
     MF = 21
     CALL LSODE (FN1, NEQ, QVAL, TI, TF, ITOL, RTOL, ATOL, ITASK, ISTATE, IOPT,
    &RWORK, LRW, IWORK, LIW, JN1, MF)
     IF (ISTATE .LT. 0) RETURN
     OSUM = 0.
          DO 4 M = 1,NT1
          Q(J,M) = QVAL(M)
          QSUM = QSUM + AN1(M) * QVAL(M)
   4
          CONTINUE
```

```
Q(J, NEQ) = QVAL(NEQ)
      QBAR(J) = QVAL(NEQ)
      US(J) = UVAL - 2.*QSUM/PHI
      ELSE
С
С
      OTHERWISE, THE INITIAL CONDITIONS ARE REINSTATED.
С
      US(J) = USP
           DO 5 M = 1, NEQ
           Q(J,M) = QO
    5
           CONTINUE
      QBAR(J) = QO
      END IF
    1 CONTINUE
      TIO = TFO
      RETURN
      END
C
      SUBROUTINE FN1(NEQ,X,Y,DY)
С
С
      THIS SUBROUTINE CALCULATES THE DERIVATIVE OF Y(I) FOR
С
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H, 0-Z)
      DIMENSION Y(NEQ), DY(NEQ)
      COMMON /SUMTRM/TERM(15,15), AN1(15), UVAL, PHI, PSI, ALFAE, NT1, NCOL1
      SUM2 = 0.
      DO 1 I = 1, NCOL1
      SUM2 = SUM2 + AN1(I)*Y(I)
      SUM1 = 0.
        DO 2 J = 1,NT1
        SUM1 = SUM1 + TERM(I,J)*Y(J)
        CONTINUE
    2
      DY(I) = SUM1
    1 CONTINUE
      DY(NT1) = (ALFAE*UVAL + 2.*SUM2*((ALFAE - 1.)*Y(NT1) - ALFAE)/PHI
     &- Y(NT1)*(2.*ALFAE*AN1(NT1)/PHI + 1. + (ALFAE - 1.)*UVAL) +
     &2.*(ALFAE - 1.)*AN1(NT1)*Y(NT1)**2/PH1)/PSI
      DY(NEQ) = 6.*(SUM2 + AN1(NT1)*Y(NT1))
      RETURN
      END
С
      SUBROUTINE JN1(NEQ,X,Y,ML,MU,PD,NRPD)
С
С
      THIS SUBROUTINE CALCULATES THE JACOBIAN MATRIX FOR
С
      SUBROUTINE LSODE.
С
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION Y(NEQ), PD(NRPD, NEQ)
      COMMON /SUMTRM/TERM(15,15), AN1(15), UVAL, PHI, PSI, ALFAE, NT1, NCOL1
      SUM2 = 0.
      DO 1 I = 1, NCOL1
```

```
SUM2 = SUM2 + AN1(I)*Y(I)
   DO 2 J = 1,NT1
   PD(I,J) = TERM(I,J)
2
  CONTINUE
1 CONTINUE
   DO 3 L = 1,NCOL1
   PD(NT1,L) = 2.*AN1(L)*((ALFAE - 1.)*Y(NT1) - ALFAE)/(PHI*PSI)
3
   CONTINUE
 PD(NT1,NT1) = (2.*((ALFAE - 1.)*SUM2 - ALFAE*AN1(NT1))/PHI - 1. -
&(ALFAE - 1.)*UVAL + 4.*(ALFAE - 1.)*AN1(NT1)*Y(NT1)/PHI)/PSI
   DO 4 L = 1,NT1
   PD(NEQ,L) = 6.*AN1(L)
  CONTINUE
4
 RETURN
 END
```

## APPENDIX C: EXPERIMENTAL DATA

. .

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Equilibrium Data

Batch Sorption Data

Fixed-Bed Data

## <u>Equilibrium Data</u>

.

Ligand: Butylamine (BA)

Equilibrium temperature: 22°C

Sample	Resin	Reagent	Equil.	Equil.	Relative
Number	weight	Amount	Conc.	Resin	Resin
	(g)	(mg)	(mg/L)	(mg)	(mg/g)
1	0.1815	13.2	34.1	9.8	54.2
2	0.2080	2.8	4.7	2.3	11.1
3	0.2218	7.0	14.6	5.5	24.7
4	0.2568	13.9	11.9	12.7	49.5
5	0.2079	20.8	35.5	17.3	83.2
6	0.2369	34.7	33.8	31.4	132.4
7	0.1957	55.6	139.7	41.6	212.6
8	0.2282	27.8	21.4	25.6	112.4
9	0.1982	41.7	63.1	35.4	178.4
10	0.2026	48.6	103.8	38.2	188.8
11	0.2232	62.5	120.9	50.4	226.0

.

## Ligand: Diglycolamine (DGA)

# Equilibrium temperature: 22°C

Sample	Resin	Reagent	Equil.	Equil.	Relative
-	Weight	Charge	Solution	Amount on	Amount on
Number		Amount	Conc.	Resin	Resin
	(g)	(mg)	(mg/L)	(mg)	(mg/g)
٦	0.2408	16.2	21.1	13.6	56.6
2	0.2346	16.2	20.9	13.7	58.3
3	0.2274	16.2	31.4	12.4	54.6
4	0.2976	16.2	24.9	13.2	44.3
5	0.2120	6.0	21.3	3.4	16.3
6	0.2817	12.0	18.0	9.8	34.9
7	0.2488	18.0	50.3	12.0	48.1
8	0.2314	22.9	44.6	17.6	76.0
9	0.2250	30.0	57.7	23.1	102.6
10	0.2719	42.0	95.8	30.5	112.2
11	0.2280	20.0	52.3	13.7	60.2
12	0.2766	30.0	61.8	22.6	81.6
13	0.2460	38.9	114.8	25.1	102.1
14	0.2588	90.7	382.1	44.9	173.4

.

## Ligand: Diglycolamine (DGA)

.

Equilibrium temperature: 50°C

Sample	Resin	Reagent	Equil.	Equil.	Relative
	Weight	Charge	Solution	Amount on	Amount on
Number		Amount	Conc.	Resin	Resin
	(g)	(mg)	(mg/L)	(mg)	(mg/g)
1	0.2196	11.6	33.0	7.7	34.9
2	0.2313	17.4	58.1	10.5	45.3
3	0.2537	7.3	9.3	6.2	24.3
4	0.2048	10.2	18.0	8.0	39.2
5	0.2575	8.0	8.6	7.0	27.0
6	0.2580	10.9	13.4	9.3	36.1
7	0.2563	13.1	25.1	10.1	39.3
8	0.2508	6.5	5.5	5.9	23.4
9	0.2590	2.7	2.5	2.4	9.2
10	0.2609	5.4	2.5	5.1	19.5
11	0.2562	7.8	25.4	4.8	18.7

### Batch Sorption Data

Ligand Exchange Batch Sorption Data - BA1

-

Temperature: 22°C

Feed Concentration: 171 mg/L

Amount of resin: 7.6944 g

Sorber solution volume: 1000 ml

Impeller rotation speed: 600 rpm

Film transfer coefficient: 4.47x10<sup>+3</sup> cm/sec

on

Ligand Exchange Batch Sorption Data - BA2

Temperature: 22°C

Feed Concentration: 171 mg/L

Amount of resin: 8.0398 g

Sorber solution volume: 1000 ml

Impeller rotation speed: 500 rpm

Film transfer coefficient: 3.53x10<sup>-3</sup> cm/sec

Sample	Sample	Ligand
Number	Time	Concentration
	(sec)	(mg/L)
1	38	143.7
2	60	132.3
3	120	105.1
4	168	82.8
5	195	77.4
6	240	75.0
7	288	57.5
8	360	48.9
9	422	43.2
10	495	33.2
11	578	25.5

Ligand Exchange Batch Sorption Data - BA3

Temperature: 22°C

.

Feed Concentration: 177 mg/L

Amount of resin: 8.0474 g

Sorber solution volume: 1000 ml

Impeller rotation speed: 600 rpm

Film transfer coefficient: 5.51x10\*3 cm/sec

Sample	Sample	Ligand
Number	Time	Concentration
	(sec)	(mg/L)
1	30	125.
2	60	116.
3	90	93.6
4	135	74.9
5	180	70.5
6	225	68.4
7	270	53.8
8	340	46.7
9	420	41.9
10	525	33.6
11	630	27.2

Ligand Exchange Batch Sorption Data - DGA1

Temperature: 22°C

Feed Concentration: 158 mg/L

Amount of resin: 8.1001 g

Sorber solution volume: 1000 ml

Impeller rotation speed: 600 rpm

Film transfer coefficient: 6.94x10<sup>-3</sup> cm/sec

Sample	Sample	Ligand
Number	Time	Concentration
	(sec)	(mg/L)
1	30	118.
2	70	89.6
3	110	79.5
4	155	64.8
5	205	62.3
6	270	36.5
7	350	26.6

Ligand Exchange Batch Sorption Data - DGA2

Temperature: 22°C

Feed Concentration: 154 mg/L

Amount of resin: 7.0232 g

Sorber solution volume: 1000 ml

Impeller rotation speed: 600 rpm

Film transfer coefficient: 3.97x10<sup>-3</sup> cm/sec

Sample	Sample	Ligand
Number	Time	Concentration
	(sec)	(mg/L)
1	30	121.
2	75	117.
3	120	91.1
4	167	76.8
5	205	71.3
6	275	45.5
7	349	42.0

Ligand Exchange Batch Sorption Data - DGA3

Temperature: 22°C

Feed Concentration: 154 mg/L

1

Amount of resin: 5.9883 g

Sorber solution volume: 1000 ml

Impeller rotation speed: 600 rpm

Film transfer coefficient: 6.46x10<sup>-3</sup> cm/sec

Sample	Sample	Ligand
Number	Time	Concentration
	(sec)	(mg/L)
1	35	120.
2	75	102.
3	200	89.5
4	270	60.3
5	340	57.8
6	420	52.4
7	570	34.3
8	660	25.0

### Fixed-Bed Data

Loading Butylamine Breakthrough Curve - BAL1

Temperature: 22°C

Loading feed concentration: 223 mg/L

Amount of resin: 2.0003 g

Resin bed length: 6.2 cm

Column diameter: 0.84 cm

Average flowrate 1.14 ml/min

Sample	Collection	Sample	Total	Volume	Ligand
Number	Time	Volume	Volume	Through	Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	1920.0	59.0	59.0	29.5	9.23
2	1920.0	44.0	103.0	81.0	9.23
3	1920.0	42.0	145.0	124.0	
4	1680.0	36.0	181.0	163.0	10.4
5	1680.0	37.0	218.0	199.5	
6	1680.0	38.0	256.0	237.0	12.7
7	1680.0	38.0	294.0	275.0	
8	1680.0	36.0	330.0	312.0	16.2
9	1680.0	36.0	366.0	348.0	
10	1920.0	47.0	413.0	389.5	11.5
11	1920.0	50.0	463.0	438.0	15.0
12	1920.0	49.0	512.0	487.5	20.8
13	1920.0	37.0	549.0	530.5	21.9
14	1920.0	38.0	587.0	568.0	
15	1920.0	39.0	626.0	606.5	25.4
16	1920.0	39.0	665.0	645.5	36.9
17	1920.0	40.0	705.0	685.0	35.8
18	1920.0	40.0	745.0	725.0	42.7
19	1920.0	42.0	787.0	766.0	48.5
20	1920.0	42.0	829.0	808.0	51.9
21	1920.0	43.0	872.0	850.5	56.6
22	1920.0	41.0	913.0	892.5	60.0
23	1920.0	40.0	953.0	933.0	63.5
24	1920.0	42.0	995.0	974.0	65.8
25	1920.0	42.0	1037.0	1016.0	75.0
26	1920.0	43.0	1080.0	1058.5	75.0
27	1920.0	42.0	1122.0	1101.0	80.8
28	1920.0	42.0	1164.0	1143.0	85.4
29	1920.0	42.0	1206.0	1185.0	93.5
30	2280.0	41.0	1247.0	1226.5	93.5
31	2280.0	78.0	1325.0	1286.0	99.3

32	2280.0	48.0	1373.0	1349.0	112.	
33	2640.0	46.0	1419.0	1396.0	118.	
34	2640.0	77.0	1496.0	1457.5	116.	
35	2640.0	46.0	1542.0	1519.0	129.	
36	2640.0	45.0	1587.0	1564.5	136.	
37	2640.0	46.0	1633.0	1610.0	136.	
38	2640.0	48.0	1681.0	1657.0		
39	2640.0	48.0	1729.0	1705.0	143.	
40	2640.0	49.0	1778.0	1753.5		
41	2640.0	49.0	1827.0	1802.5	150.	
42	2640.0	49.0	1876.0	1851.5		
43	2640.0	46.0	1922.0	1899.0	154.	
44	2640.0	46.0	1968.0	1945.0	154.	
45	2640.0	50.0	2018.0	1993.0		
46	1140.0	31.0	2049.0	2033.5	163.	
47	2640.0	39.0	2088.0	2068.5		
· 48	2640.0	38.0	2126.0	2107.0	154.	
49	2640.0	38.0	2164.0	2145.0		
50	2640.0	35.0	2199.0	2181.5		
51	2640.0	33.0	2232.0	2215.5	152.	
52	2640.0	33.0	2265.0	2248.5		
53	2640.0	36.0	2301.0	2283.0		
54	2640.0	38.0	2339.0	2320.0	158.	
55	2640.0	38.0	2377.0	2358.0		
56	2640.0	39.0	2416.0	2396.5		
57	2640.0	41.0	2457.0	2436.5	165.	
58	2640.0	40.0	2497.0	2477.0		
59	2640.0	38.0	2535.0	2516.0		
60	2640.0	38.0	2573.0	2554.0	166.	
61	2640.0	40.0	2613.0	2593.0		
62	2640.0	37.0	2650.0	2631.5		
63	2640.0	39.0	2689.0	2669.5	167.	
64	2640.0	37.0	2726.0	2707.5	168.	
65	2640.0	36.0	2762.0	2744.0		
66	2640.0	35.0	2797.0	2779.5		
67	2640.0	36.0	2833.0	2815.0	170.	
68	2640.0	36.0	2869.0	2851.0		
69	2640.0	35.0	2904.0	2886.5		
70	2640.0	35.0	2939.0	2921.5	165.	
71	2640.0	34.0	2973.0	2956.0		
72	2640.0	35.0	3008.0	2990.5		
73	2640.0	35.0	3043.0	3025.5	173.	
74	2640.0	35.0	3078.0	3060.5		
75	2640.0	35.0	3113.0	3095.5		
76	2640.0	36.0	3149.0	3131.0	168.	
77	2640.0	55.0	3204.0	3176.5		
78	2640.0	52.0	3256.0	3230.0		
79	2640.0	49.0	3305.0	3280.5	181.	
80	2640.0	55.0	3360.0	3332.5		
81	2640.0	58.0	3418.0	3389.0		
82	2640.0	58.0	3476.0	3447.0	181.	
83	2640.0	59.0	3535.0	3505.5		

84	2640.0	59.0	3594.0	3564.5	
85	2640.0	59.0	3653.0	3623.5	185.
86	2640.0	60.0	3713.0	3683.0	
87	2640.0	58.0	3771.0	3742.0	
88	2640.0	57.0	3828.0	3799.5	192.
89	2640.0	77.0	3905.0	3866.5	
90	2640.0	60.0	3965.0	3935.0	
91	2640.0	62.0	4027.0	3996.0	
92	2640.0	60.0	4087.0	4057.0	
93	2640.0	62.0	4149.0	4118.0	187.
94	2640.0	59.0	4208.0	4178.5	
95	2640.0	64.0	4272.0	4240.0	
96	2640.0	56.0	4328.0	4300.0	190.
97	2640.0	54.0	4382.0	4355.0	
98	2640.0	53.0	4435.0	4408.5	
99	2640.0	52.0	4487.0	4461.0	
100	2640.0	53.0	4540.0	4513.5	194.
101	2640.0	50.0	4590.0	<b>4565.0</b>	
102	2640.0	49.0	4639.0	4614.5	
103	2640.0	54.0	4693.0	4666.0	194.
104	2640.0	50.0	4743.0	4718.0	
105	2640.0	48.0	4791.0	4767.0	
106	2640.0	48.0	4839.0	4815.0	193.
107	720.0	15.0	4854.0	4846.5	

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Loading Butylamine Breakthrough Curve - BAL2

Temperature: 22°C

Loading feed concentration: 195 mg/L

Amount of resin: 1.9302 g

Resin bed length: 6.2 cm

Column diameter: 0.84 cm

Average flowrate 1.26 ml/min

Sample	Collection	Sample	Total	Volume	Ligand
Number	Time	Volume	Volume	Through	Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	1980.0	44.0	44.0	22.0	
2	1980.0	49.0	93.0	68.5	
3	1980.0	55.0	148.0	120.5	
4	1980.0	45.0	193.0	170.5	
5	1980.0	39.0	232.0	212.5	
6	1980.0	46.0	278.0	255.0	
7	1980.0	48.0	326.0	302.0	
8	1980.0	49.0	375.0	350.5	
9	1980.0	43.0	418.0	396.5	
10	1980.0	44.0	462.0	440.0	
11	1980.0	45.0	507.0	484.5	
12	1980.0	44.0	551.0	529.0	5.00
13	1980.0	45.0	596.0	573.5	
14	1980.0	45.0	641.0	618.5	5.00
15	1980.0	47.0	688.0	664.5	
16	1980.0	49.0	737.0	712.5	6.99
17	1980.0	49.0	786.0	761.5	
18	1980.0	52.0	838.0	812.0	11.0
19	1980.0	50.0	888.0	863.0	17.0
20	1980.0	48.0	936.0	912.0	19.0
21	1980.0	46.0	982.0	959.0	24.0
22	1980.0	49.0	1031.0	1006.5	28.0
23	1980.0	50.0	1081.0	1056.0	35.0
24	1980.0	50.0	1131.0	1106.0	42.0
25	1980.0	50.0	1181.0	1156.0	48.0
26	1980.0	44.0	1225.0	1203.0	54.0
27	1980.0	45.0	1270.0	1247.5	57.0
28	1980.0	49.0	1319.0	1294.5	66.0
29	1980.0	49.0	1368.0	1343.5	75.0
30	2280.0	47.0	1415.0	1391.5	83.0
31	2280.0	45.0	1460.0	1437.5	83.0
32	2280.0	45.0	1505.0	1482.5	86.0

33	2640.0	47.0	1552.0	1528.5	89.0
34	2640.0	46.0	1598.0	1575.0	96.0
35	2640.0	45.0	1643.0	1620.5	98.0
36	2640.0	44.0	1687.0	1665.0	
37	2640.0	45.0	1732.0	1709.5	105.
38	2640.0	45.0	1777.0	1754.5	
39	2640.0	45.0	1822.0	1799.5	112.
40	2640.0	45.0	1867.0	1844.5	
40	2640 0	43.0	1914.0	1890.5	117.
A2	2640.0	45.0	1959 0	1936 5	
13	2640.0	45.0	2004 0	1981 5	123
43	2640.0	43.0	2051 0	2027 5	125.
44	2040.0	47.0	2031.0	2027.5	123.
43	2040.0	43.0	2030.0	2073.5	120.
40	2640.0	43.0	2191 0	2140 0	125
4/	2640.0	42.0	2101.0	2100.0	125.
48	2640.0	41.0	2222.0	2201.5	107
49	2640.0	49.0	22/1.0	2240.5	127.
50	2640.0	47.0	2318.0	2294.5	133.
51	2640.0	46.0	2364.0	2341.0	
52	2640.0	47.0	2411.0	2387.5	133.
53	2640.0	46.0	2457.0	2434.0	
54	2640.0	50.0	2507.0	2482.0	136.
55	2640.0	48.0	2555.0	2531.0	
56	2640.0	47.0	2602.0	2578.5	138.
57	2640.0	49.0	2651.0	2626.5	139.
58	2640.0	52.0	2703.0	2677.0	146.
59	2640.0	54.0	2757.0	2730.0	144.
60	2640.0	53.0	2810.0	2783.5	
61	2640.0	56.0	2866.0	2838.0	148.
62	2640.0	52.0	2918.0	2892.0	
63	2640.0	50.0	2968.0	2943.0	
64	2640.0	52.0	3020.0	2994.0	152.
65	2640.0	53.0	3073.0	3046.5	
66	2640.0	54.0	3127.0	3100.0	
67	2640.0	52.0	3179.0	3153.0	157.
68	2640.0	52.0	3231.0	3205.0	
69	2640.0	51.0	3282.0	3256.5	
70	2640.0	50.0	3332.0	3307.0	157.
71	2640.0	49.0	3381.0	3356.5	
72	2640.0	48.0	3429.0	3405.0	
73	2640.0	48.0	3477.0	3453.0	159.
74	2640.0	50.0	3527.0	3502.0	
75	2640.0	49.0	3576.0	3551.5	
76	2640.0	50.0	3626.0	3601.0	162.
77	2640.0	48.0	3674.0	3650.0	
78	2640.0	48.0	3722.0	3698.0	
79	2640.0	51.0	3773.0	3747.5	161.
80	2640.0	50.0	3823.0	3798.0	
81	2640.0	49.0	3872.0	3847.5	
82	2640.0	50.0	3922.0	3897-0	165.
83	2640.0	48.0	3970.0	3946.0	
84	2640.0	48.0	4018.0	3994.0	166.
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85	2640.0	47.0	4065.0	4041.5		
86	2640.0	47.0	4112.0	4088.5		•
87	2160.0	52.0	4164.0	4138.0	167.	
88	2160.0	53.0	4217.0	4190.5		
89	2160.0	55.0	4272.0	4244.5		
90	2160.0	56.0	4328.0	4300.0	170.	
91	2160.0	56.0	4384.0	4356.0		
92	2160.0	57.0	4441.0	4412.5		
93	2160.0	57.0	4498.0	4469.5	172.	
94	2160.0	56.0	4554.0	4526.0		
95	2160.0	54.0	4608.0	4581.0		_
96	2160.0	58.0	4666.0	4637.0	172.	•
97	2160.0	55.0	4721.0	4693.5		
98	2160.0	54.0	4775.0	4748.0		
99	2160.0	54.0	4829.0	4802.0	173.	
100	2160.0	56.0	4885.0	4857.0		
101	2160.0	57.0	4942.0	4913.5		
102	2160.0	57.0	4999.0	4970.5		
103	2160.0	58.0	5057.0	5028.0		
104	2160.0	61.0	5118.0	5087.5		
105	2160.0	54.0	5172.0	5145.0	178.	
106	2160.0	53.0	5225.0	5198.5		
107	2160.0	52.0	5277.0	5251.0	177.	
108	1712.0	15.0	5292.0	5284.5		

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Loading Butylamine Breakthrough Curve - BAL3

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Temperature: 22°C

Loading feed concentration: 190 mg/L

Amount of resin: 2.0349 g

Resin bed length: 6.2 cm

Column diameter: 1.08 cm

Average flowrate 1.06 ml/min

Sample Number	Collection Time	Sample Volume	Total Volume	Volume Through	Ligand Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	1920.0	21.0	21.0	10.5	
2	1920.0	55.0	76.0	48.5	1.94
3	1920.0	50.0	126.0	101.0	
4	1920.0	42.0	168.0	147.0	4.85
5	1920.0	39.0	207.0	187.5	
6	1920.0	44.0	251.0	229.0	0.00
7	1920.0	44.0	295.0	273.0	
8	1920.0	47.0	342.0	318.5	
9	1920.0	72.0	414.0	378.0	
10	1920.0	37.0	451.0	432.5	
11	1920.0	39.0	490.0	470.5	0.00
12	1920.0	33.0	523.0	506.5	
13	1920.0	34.0	557.0	540.0	
14	1920.0	36.0	593.0	575.0	0.00
15	1920.0	38.0	631.0	612.0	
16	1920.0	39.0	670.0	650.5	
17	1920.0	40.0	710.0	690.0	0.00
18	1920.0	43.0	753.0	731.5	
19	1920.0	43.0	796.0	774.5	
20	1920.0	45.0	841.0	818.5	0.97
21	1920.0	43.0	884.0	862.5	
22	1920.0	45.0	929.0	906.5	
23	1920.0	44.0	973.0	951.0	5.82
24	1920.0	45.0	1018.0	995.5	
25	1920.0	41.0	1059.0	1038.5	
26	1920.0	29.0	1088.0	1073.5	8.73
27	1920.0	31.0	1119.0	1103.5	
28	1920.0	33.0	1152.0	1135.5	
29	1920.0	33.0	1185.0	1168.5	12.6
30	1920.0	33.0	1218.0	1201.5	13.6
31	1920.0	32.0	1250.0	1234.0	
32	1920.0	33.0	1283.0	1266.5	17.5

33	1920.0	34.0	1317.0	1300.0	
34	1920.0	32.0	1349.0	1333.0	~~~~~
35	1920.0	33.0	1382.0	1365.5	
36	1920.0	34.0	1416.0	1399.0	
37	1920.0	33.0	1449.0	1432.5	31.0
38	1920.0	32.0	1481.0	1465.0	28.1
39	1920.0	34.0	1515.0	1498.0	30.1
40	1920.0	36.0	1551.0	1533.0	
41	1920.0	35.0	1586.0	1568.5	32.0
42	1920.0	35.0	1621.0	1603.5	34.0
43	1920.0	35.0	1656.0	1638.5	38.8
44	1920.0	36.0	1692.0	1674.0	42.7
45	1920.0	37.0	1729.0	1710.5	42.7
46	1920.0	38.0	1767.0	1748.0	50.4
47	1920.0	38.0	1805.0	1786.0	50.4
48	1920.0	38.0	1843.0	1824.0	56.3
49	1920.0	42.0	1885.0	1864.0	60.2
50	1920.0	40.0	1925.0	1905.0	63.1
51	1920-0	41.0	1966.0	1945.5	66.0
52	1920.0	45.0	2011 0	1988.5	72.8
52	1920.0	47.0	2058.0	2034 5	83.4
50	1920.0	49.0	2107 0	2082 5	87.3
54	2460 0	52 0	2159 0	2133 0	95 1
55 66	2400.0	42 0	2201 0	2180 0	90.2
50	2400.0	42.0	2201.0	22222 0	83 A
57	2460.0	52.0	2243.0	2260 5	89.3
50	2460.0		2290.0	2200.5	95.5
59	2460.0	49.0 52 A	2345.0	2371 0	99.1
61	2460.0	52.0	2397.0	2422 0	
62	2400.0	52.0	2501 0	2425.0	
62	2460.0	52.0	2552 0	2527 0	108
63	2460.0	52.0	2555.0	2579 0	100.
65	2460.0	52.0	2605.0	2630 0	109.
60	2460.0	50.0	2055.0	2692 5	11/
20	2400.0	55.0	2710.0	2736 5	114.
67	2400.0	53.0	2703.0	2730.5	117
60	2400.0	53.0	2010.0	2003.5	11/.
70	2400.0	32.0	2000.0	2042.0	117
70	2400.0	40.0	2910.0	2072.0	
/1	2400.0	44.0	2960.0	2930.0	
12	2460.0	44.0	3004.0	2702.0	110
/3	2460.0	45.0	3049.0	3020.5	119.
74 75	2460.0	41.0	3090.0	2112 0	
75	2460.0	44.0	3134.0	3112.0	100
76	2460.0	43.0	3177.0	3155.5	123.
77	2460.0	44.0	3221.0	3199.0	
78	2460.0	43.0	3264.0	3242.5	100
79	2460.0	43.0	3307.0	3285.5	126.
80	2460.0	41.0	3348.0	3327.5	
81	2460.0	39.0	3387.0	3367.5	
82	2460.0	39.0	3426.0	3406.5	125.
83	2460.0	40.0	3466.0	3446.0	
84	2460.0	38.0	3504.0	3485.0	

OF	2460 0	20 0	2542 0	2522 0	128	
00	2400.0	38.0	3542.0	2522.0	120.	
86	3060.0	43.0	3585.0	3563.5		
87	3060.0	46.0	3631.0	3608.0		
88	3060.0	48.0	3679.0	3655.0	130.	
89	3060.0	46.0	3725.0	3702.0		
90	3060.0	47.0	3772.0	3748.5	130.	
91	3060.0	49.0	3821.0	3796.5		
92	3060.0	50.0	3871.0	3846.0		
<del>9</del> 3 ·	3060.0	46.0	3917.0	3894.0	137.	•
94	3060.0	47.0	3964.0	3940.5		
95	3060.0	46.0	4010.0	3987.0		
96	3060.0	45.0	4055.0	4032.5	138.	
97	3060.0	45.0	4100.0	4077.5		
98	3060.0	42.0	4142.0	4121.0		
99	3060.0	36.0	4178.0	4160.0		
100	3060.0	40.0	4218.0	4198.0	137.	
101	3060.0	40.0	4258.0	4238.0		
102	3060.0	42.0	4300.0	4279.0		
103	3060.0	41.0	4341.0	4320.5		
104	3060.0	38.0	4379.0	4360.0		
105	3060.0	38.0	4417.0	4398.0		
106	3060.0	33.0	4450.0	4433.5	143.	
107	3060.0	34.0	4484.0	4467.0		
108	3060.0	35.0	4519.0	4501.5		
109	3060.0	37.0	4556.0	4537.5		
110	3060.0	35.0	4591.0	4573.5		
111	3060.0	37.0	4628.0	4609.5		
112	3060.0	39.0	4667.0	4647.5	146.	
113	3060.0	48.0	4715.0	4691.0		
114	3060.0	63.0	4778.0	4746.5	155.	
115	3060.0	61.0	4839.0	4808.5	~~~~	

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Temperature: 22°C

Loading feed concentration: 164 mg/L

Amount of resin: 2.3628 g

Resin bed length: 8.6 cm

Column diameter: 0.84 cm

Average flowrate 1.94 ml/min

Sample	Collection Time	Sample Volume	Total Volume	Volume Through	Ligand Conc.
Manaser	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	1980.0	13.4	13.4	6.7	
2	1980.0	63.0	76.4	44.9	
3	1980.0	63.0	139.4	107.9	
4	1980.0	63.0	202.4	170.9	
5	1980.0	63.0	265.4	233.9	
6	1980.0	63.0	328.4	296.9	
7	1980.0	63.0	391.4	359.9	
8	1980.0	63.0	454.4	422.9	
9	1980.0	70.0	524.4	489.4	26.0
10	1980.0	71.0	595.4	559.9	29.6
11	1980.0	71.0	666.4	630.9	27.8
12	1980.0	56.0	722.4	694.4	32:3
13	1980.0	52.0	774.4	748.4	27.8
14	1980.0	53.0	827.4	800.9	28.7
15	1980.0	54.0	881.4	854.4	30.5
16	1980.0	51.0	932.4	906.9	30.5
17	1980.0	54.0	986.4	959.4	28.7
18	1980.0	55.0	1041.4	1013.9	31.4
19	1980.0	55.0	1096.4	1068.9	37.7
20	1980.0	58.0	1154.4	1125.4	39.5
21	1980.0	55.0	1209.4	1181.9	35.9
22	1980.0	58.0	1267.4	1238.4	38.6
23	1980.0	60.0	1327.4	1297.4	37.7
24	1980.0	60.0	1387.4	1357.4	39.5
25	1980.0	61.0	1448.4	1417.9	50.2
26	1980.0	68.0	1516.4	1482.4	44.0
27	1980.0	75.0	1591.4	1553.9	49.4
28	1980.0	69.0	1660.4	1625.9	54.7
29	1980.0	66.0	1726.4	1693.4	53.8
30	1980.0	63.0	1789.4	1757.9	56.5
31	1980.0	54.0	1843.4	1816.4	55.6
32	1980.0	74.0	1917.4	1880.4	66.4

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33	1980.0	69.0	1986.4	1951.9	79.9
34	1980.0	68.0	2054.4	2020.4	79.9
35	1980.0	74.0	2128.4	2091.4	84.4
36	1980.0	76.0	2204.4	2166.4	90.6
37	1980.0	77.0	2281.4	2242.9	104.
38	1980.0	77.0	2358.4	2319.9	99.6
39	1980.0	77.0	2435.4	2396.9	114.
40	1980.0	77.0	2512.4	2473.9	103.
41	1980.0	77.Ó	2589.4	2550.9	125.
42	2100.0	71.0	2660.4	2624.9	117.
43	1980.0	67.0	2727.4	2693.9	118.
44	1980.0	73.0	2800.4	2763.9	118.
45	1980.0	75.0	2875.4	2837.9	114.
46	1980.0	70.0	2945.4	2910.4	121.
47	1980.0	69.0	3014.4	2979.9	119.
48	1980.0	72.0	3086.4	3050.4	128.
49	1980.0	73.0	3159.4	3122.9	126.
50	1980.0	77.0	3236.4	3197.9	136.

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Temperature: 22°C

Loading feed concentration: 164 mg/L

Amount of resin: 2.3800 g

Resin bed length: 8.6 cm

Column diameter: 0.84 cm

Average flowrate 0.986 ml/min

Sample	Collection	Sample	Total	Volume	Ligand
Number	Time	Volume	Volume	Through	Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	2780 0	27 0	27 0	12 E	19.9
1	3180.0	27.0	27.0	13.5	7 1 2
2	3100.0	60.0	164.0	124 0	9.09
3	3/00.0	60.0	104.0	109 5	11 7
4 E	3420.0	69.0	233.0	190.5	10.2
5	3780.0	70.0	299.0	200.0	10.3
6	3780.0	78.0	377.0	330.0	3.0/
<i>'</i>	3780.0	51.0	420.0	402.3	14.4
8	3780.0	51.0	4/9.0	453.5	9.42
9	3780.0	51.0	540.0	509.5	11.7
10	3780.0	72.0	612.0	5/0.0	10.9
11	3780.0	75.0	687.0	649.5	10.0
12	3780.0	42.0	729.0	708.0	11.7
13	3780.0	68.0	/9/.0	763.0	14.4
14	3780.0	59.0	856.0	826.5	11.7
15	2160.0	35.0	891.0	8/3.5	18.0
16	2160.0	30.0	921.0	906.0	13.5
17	2160.0	28.0	949.0	935.0	13.5
18	2160.0	32.0	981.0	965.0	14.4
19	2160.0	34.0	1015.0	998.0	21.5
20	2160.0	29.0	1044.0	1029.5	24.2
21	2160.0	31.0	1075.0	1059.5	19.7
22	2160.0	31.0	1106.0	1090.5	24.2
23	2160.0	31.0	1137.0	1121.5	20.6
24	2160.0	28.0	1165.0	1151.0	19.7
25	2160.0	28.0	1193.0	1179.0	26.0
26	4320.0	56.0	1249.0	1221.0	11.7
27	4320.0	60.0	1309.0	1279.0	7.18
28	4320.0	59.0	1368.0	1338.5	14.4
29	3360.0	50.0	1418.0	1393.0	15.3
30	3360.0	57.0	1475.0	1446.5	13.5
31	3360.0	58.0	1533.0	1504.0	11.7
32	3360.0	61.0	1594.0	1563.5	13.5

33	3360.0	66.0	1660.0	1627.0	13.5
34	3360.0	67.0	1727.0	1693.5	13.5
35	3360.0	61.0	1788.0	1757.5	12.6
36	3360.0	57.0	1845.0	1816.5	17.0
37	3360.0	56.0	1901.0	1873.0	18.0
38	3360.0	61.0	1962.0	1931.5	20.6
39	3360.0	69.0	2031.0	1996.5	20.6
40	3360.0	71.0	2102.0	2066.5	23.3
41	3360.0	52.0	2154.0	2128.0	26.0
42	3360.0	53.0	2207.0	2180.5	26.9
43	3360.0	54.0	2261.0	2234.0	28.7
44	3360.0	50.0	2311.0	2286.0	24.2
45	3360.0	50.0	2361.0	2336.0	37.2
46	3360.0	47.0	2408.0	2384.5	38.6
47	3360.0	43.0	2451.0	2429.5	42.0
48	3360.0	39.0	2490.0	2470.5	° 38.8
49	3360.0	37.0	2527.0	2508.5	42.2
50	3360.0	38.0	2565.0	2546.0	49.4
51	3360.0	38.0	2603.0	2584.0	49.4
52	3360.0	40.0	2643.0	2623.0	50.2
53	3360.0	40.0	2683.0	2663.0	58.3
54	3360.0	45.0	2728.0	2705.5	58.3
55	3360.0	67.0	2795.0	2761.5	76.3
56	3360.0	68.0	2863.0	2829.0	88.8
57	3360.0	64.0	2927.0	2895.0	96.9
58	3360.0	53.0	2980.0	2953.5	93.3
59	3360.0	44.0	3024.0	3002.0	96.0
60	3360.0	45.0	3069.0	3046.5	98.7
61	3360.0	51.0	3120.0	3094.5	98.7
62	3360.0	63.0	3183.0	3151.5	102.
63	3360.0	62.0	3245.0	3214.0	109.
64	3360.0	73.0	3318.0	3281.5	118.
65	3360.0	76.0	3394.0	3356.0	126.
66	3360.0	75.0	3469.0	3431.5	127.
67	3360.0	75.0	3544.0	3506.5	128.
68	3360.0	73.0	3617.0	3580.5	134.
69	3360.0	42.0	3659.0	3638.0	128.
70	3360.0	72.0	3731.0	3695.0	118.
71	3360.0	66.0	3797.0	3764.0	113.
72	3360.0	64.0	3861.0	3829.0	115.
73	3360.0	61.0	3922.0	3891.5	113.
74	3360.0	69.0	3991.0	3956.5	117.
75	3360.0	54.0	4045.0	4018.0	121.
76	2700.0	68.0	4113.0	4079.0	138.
77	3360.0	64.0	4177.0	4145.0	155.
78	3360.0	64.0	4241.0	4209.0	144.

Temperature: 22°C

Loading feed concentration: 178 mg/L

Amount of resin: 1.4781 g

Resin bed length: 5.1 cm

Column diameter: 0.84 cm

Average flowrate 1.43 ml/min

Sample	Collection	Sample	Total	Volume	Ligand
Number	Time	Volume	Volume	Through	Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
	0100 0	<b>60 0</b>	<b>60 0</b>	24.0	0.42
1	2100.0	68.0	146 0	107.0	9.42
2	2100.0	78.0	140.0	107.0	10./
3	2100.0	78.0	224.0	105.0	3.14
4	2100.0	78.0	302.0	203.0	10.4
5	2100.0	48.0	350.0	320.0	27.0
6	2100.0	51.0	401.0	3/3.3	10.0
7	2100.0	52.0	453.0	427.0	10.0
8	2100.0	51.0	504.0	4/0.5	23.8
9	2100.0	55.0	559.0	531.5	29.2
10	2100.0	56.0	615.0	567.0	20.0
11	2100.0	59.0	674.0	044.3	32.8
12	2100.0	62.0	736.0	705.0	41.7
13	2100.0	49.0	785.0	760.5	44.4
14	2100.0	50.0	835.0	810.0	44.4
15	2100.0	51.0	886.0	860.5	48.9
16	2100.0	52.0	938.0	912.0	56.1
17	2100.0	59.0	997.0	967.5	63.3
18	2100.0	60.0	1057.0	1027.0	66.8
19	2100.0	57.0	1114.0	1085.5	74.9
20	2100.0	60.0	1174.0	1144.0	74.0
21	2100.0	47.0	1221.0	1197.5	72.2
22	2100.0	47.0	1268.0	1244.5	72.2
23	2100.0	47.0	1315.0	1291.5	76.7
24	2100.0	47.0	1362.0	1338.5	74.9
25	2100.0	48.0	1410.0	1386.0	81.2
26	2120.0	48.0	1458.0	1434.0	83.9
27	2100.0	46.0	1504.0	1481.0	85.7
28	2100.0	47.0	1551.0	1527.5	85.7
29	2100.0	47.0	1598.0	1574.5	93.8
30	2100.0	47.0	1645.0	1621.5	101.
31	2100.0	48.0	1693.0	1669.0	100.
32	2100.0	50.0	1743.0	1718.0	106.

33	2100.0	49.0	1792.0	1767.5	110.
34	2100.0	51.0	1843.0	1817.5	114.
35	2100.0	50.0	1893.0	1868.0	115.
36	2100.0	50.0	1943.0	1918.0	120.
37	2100.0	55.0	1998.0	1970.5	124.
38	2100.0	57.0	2055.0	2026.5	130.
39	2100.0	58.0	2113.0	2084.0	134.
40	2100.0	61.0	2174.0	2143.5	136.
40	2100.0	52 0	2226.0	2200.0	138.
41 42	2100.0	52.0	2278 0	2252.0	136
46	2100.0	52.0	2331 0	2202.0	137
43	2100.0	53.0	2384 0	2367 5	140
44	2100.0	55.0	2/30 0	2007.0	143
40 AC	2100.0	55.0	2435.0	2411.5	144
40	2100.0	57.0	2490.0	2524 0	144.
41	2100.0	50.0	2552.0	2524.0	144.
40	2100.0	50.0	2000.0	2500.0	140.
47	2100.0	50.0	2030.0	2633.0	140.
50	2100.0	51.0	2761 0	2725 0	149.
57	2100.0	52.0	2701.0	2733.0	
52	2100.0	51.0	2012.0	2227 5	148
55	2100.0	AO 0	2003.0	2037.5	170.
24 55	2100.0	49.0	2912.0	2036 0	
55	2100.0	40.0	3006.0	2983 0	150
50	2100.0	40.0	3053 0	3029 5	
57	2100.0	51 0	3104 0	3078 5	
50	2100.0	54 0	3158 0	3131 0	152
60	2100.0	52.0	3210 0	3184 0	
61	2100.0	45 0	3255 0	3232 5	
62	2100.0	43.0	3299.0	3277 0	154
63	2100.0	42.0	3341 0	3320.0	
64	2100.0	42.0	3382.0	3361.5	
65	2100.0	41 0	3423 0	3402 5	154
66	2100.0	40.0	3463.0	3443.0	
67	2100.0	37 0	3500.0	3481.5	
68	2100.0	37.0	3537.0	3518.5	153.
69	2100.0	37.0	3574.0	3555.5	
70	2100.0	38.0	3612.0	3593.0	
70	2100.0	39.0	3651.0	3631.5	155.
72	2100.0	37.0	3688.0	3669.5	
73	2100.0	38.0	3726.0	3707.0	
74	2100.0	39.0	3765.0	3745.5	
75	2100.0	40 0	3805.0	3785.0	159.
76	2100.0	43 0	3848-0	3826.5	166.
77	2100.0	45.0	3893-0	3870.5	
78	2100.0	45.0	3938.0	3915.5	166.
79	2100.0	45.0	3983.0	3960.5	
80	2100.0	45.0	4028-0	4005.5	170.
~~	<b>DI</b>	-10.0			

Temperature: 22°C

Loading feed concentration: 162 mg/L

Amount of resin: 2.013 g

Resin bed length: 6.2 cm

Column diameter: 1.08 cm

Average flowrate 1.55 ml/min

Sample Number	Collection Time (coc)	Sample Volume	Total Volume	Volume Through	Ligand Conc.
	(360)	()	(112)		(
1	2760.0	70.0	70.0	35.0	3.33
2	2760.0	38.8	108.8	89.4	6.33
3	2760.0	35.8	144.6	126.7	
4	2760.0	35.2	179.8	162.2	
5	2760.0	73.0	252.8	216.3	8.33
6	2021.0	64.0	316.8	284.8	9.99
7	2100.0	75.0	391.8	354.3	13.3
8	2100.0	67.0	458.8	425.3	16.6
9	2100.0	57.5	516.3	487.5	11.7
10	2100.0	56.5	572.8	544.5	13.3
11	2100.0	57.0	629.8	601.3	13.3
12	2100.0	51.5	681.3	655.5	16.6
13	2100.0	50.8	732.1	706.7	16.6
14	2100.0	75.0	807.1	769.6	
15	2100.0	49.5	856.6	831.8	16.6
16	2100.0	46.0	902.6	879.6	13.3
17	2100.0	45.0	947.6	925.1	20.0
18	2100.0	44.0	991.6	969.6	
19	2100.0	43.8	1035.4	1013.5	20.0
20	2100.0	69.0	1104.4	1069.9	
21	2100.0	45.0	1149.4	1126.9	20.0
22	2100.0	70.0	1219.4	1184.4	
23	2100.0	44.5	1263.9	1241.6	20.0
24	2100.0	69.5	1333.4	1298.6	
25	2100.0	44.0	1377.4	1355.4	25.0
26	2100.0	69.0	1446.4	1411.9	
27	2100.0	66.0	1512.4	1479.4	
28	2100.0	40.0	1552.4	1532.4	30.0
29	2100.0	58.0	1610.4	1581.4	
30	2100.0	45.0	1655.4	1632.9	
31	2100.0	44.0	1699.4	1677.4	31.6
32	2100.0	54.5	1753.9	1726.6	43.3

33	2100.0	74.8	1828.7	1791.3	
34	2100.0	51.0	1879.7	1854.2	48.3
35	2100.0	56.5	1936.2	1907.9	55.0
36	2100.0	56.9	1993.1	1964.6	56.6
37	2100.0	56.0	2049.1	2021.1	61.6
38	2100.0	38.0	2087.1	2068.1	61.6
39	2100.0	73.5	2160.6	2123.8	
40	2100.0	52.0	2212.6	2186.6	61.6
41	2100.0	60.0	2272.6	2242.6	76.6
42	2100.0	76.0	2348.6	2310.6	103.
43	2100.0	74.8	2423.4	2386.0	100.
44	2100.0	62.8	2486.2	2454.8	102.
45	1620.0	37.0	2523.2	2504.7	91.6

Temperature: 22°C

Loading feed concentration: 167 mg/L

Amount of resin: 3.1694 g

Resin bed length: 8.1 cm

Column diameter: 1.08 cm

Average flowrate 1.12 ml/min

Sample Number	Collection Time	Sample Volume	Total Volume	Volume Through	Ligand Conc.
Truino er	(sec)	(ml)	(ml)	(ml)	(mg/L)
-			40.0		
1	2160.0	40.0	40.0	20.0	
2	2160.0	49.0	89.0	64.5	5.43
3	2160.0	55.0	144.0	116.5	
4	2160.0	26.0	170.0	157.0	8.15
5	2160.0	49.0	219.0	194.5	
6	2160.0	55.0	274.0	246.5	11.8
7	2160.0	45.0	319.0	296.5	
8	2160.0	38.0	357.0	338.0	18.1
9	2160.0	28.0	385.0	371.0	
10	2160.0	46.0	431.0	408.0	26.3
11	2160.0	45.0	476.0	453.5	
12	2160.0	47.0	523.0	499.5	20.8
13	2160.0	47.0	570.0	546.5	
14	2160.0	50.0	620.0	595.0	20.8
15	2160.0	49.0	669.0	644.5	
16	2160.0	51.0	720.0	694.5	
17	2160.0	53.0	773.0	746.5	15.4
18	2160.0	53.0	826.0	799.5	
19	2160.0	52.0	878.0	852.0	
20	2160.0	50.0	928.0	903.0	11.8
21	2160.0	49.0	977.0	952.5	12.7
22	2160.0	52.0	1029.0	1003.0	
23	2160.0	51.0	1080.0	1054.5	
24	2160.0	46.0	1126.0	1103.0	17.2
25	2880.0	50.0	1176.0	1151.0	
26	2880.0	53.0	1229.0	1202.5	
27	2880.0	53.0	1282.0	1255.5	10.0
28	2880.0	52.0	1334.0	1308.0	
29	2880.0	52.0	1386.0	1360.0	
30	2880.0	55.0	1441.0	1413.5	15.4
31	2880.0	56.0	1497.0	1469.0	
32	2880.0	54.0	1551.0	1524.0	

33	2880.0	55.0	1606.0	1578.5	14.5
34	2880.0	60.0	1666.0	1636.0	
35	2880.0	60.0	1726.0	1696.0	
36	2880.0	55.0	1781.0	1753.5	25.4
37	2880.0	45.0	1826.0	1803.5	
38	2880.0	47.0	1873.0	1849.5	
39	2880.0	57.0	1930.0	1901.5	23.6
40	2880.0	55.0	1985.0	1957.5	
41	2880.0	59.0	2044.0	2014.5	
42	2880.0	57.0	2101.0	2072.5	29.9
43	2880.0	66.0	2167.0	2134.0	
44	1860.0	42.0	2209.0	2188.0	
45	2880.0	44.0	2253.0	2231.0	
46	2880.0	49.0	2302.0	2277.5	48.0
47	2880.0	53.0	2355.0	2328.5	
48	2880.0	54.0	2409.0	2382.0	57.1
49	2880.0	52.0	2461.0	2435.0	
50	2880.0	59.0	2520.0	2490.5	66.1
51	2880.0	51.0	2571.0	2545.5	
52	2880.0	50.0	2621.0	2596.0	
53	2880.0	51.0	2672.0	2646.5	78.8
54	2880.0	48.0	2720.0	2696.0	
55	2880.0	52.0	2772.0	2746.0	
56	2880.0	52.0	2824.0	2798.0	
57	2880.0	49.0	2873.0	2848.5	84.2
58	2880.0	43.0	2916.0	2894.5	
59	2880.0	43.0	2959.0	2937.5	
60	2880.0	44.0	3003.0	2981.0	87.8
61	2880.0	44.0	3047.0	3025.0	
62	2880.0	42.0	3089.0	3068.0	
63	2880.0	47.0	3136.0	3112.5	98.7
64	2880.0	47.0	3183.0	3159.5	
65	2880.0	48.0	3231.0	3207.0	
66	2880.0	44.0	3275.0	3253.0	105.
67	2880.0	47.0	3322.0	3298.5	
68	2880.0	44.0	3366.0	3344.0	
69	2880.0	51.0	3417.0	3391.5	102.
70	2880.0	50.0	3467.0	3442.0	
71	2880.0	49.0	3516.0	3491.5	118.

Regeneration of Diglycolamine Column DGAL1 - DGAR1

Temperature: 52°C

Initial bed concentration: 164 mg/L

Amount of resin: 2.3628 g

Resin bed length: 8.6 cm

Column diameter: 0.84 cm

Average flowrate 2.02 ml/min

Sample Number	Collection Time	Sample Volume	Total Volume	Volume Through	Ligand Conc.
	(sec)	<u>(</u> m⊥)	(mr)	(mr)	(mg/L)
1	420.0	13.0	13.0	6.5	129.
2	420.0	13.0	26.0	19.5	114.
3	420.0	14.0	40.0	33.0	102.
4	420.0	15.0	55.0	47.5	90.9
5	420.0	17.0	72.0	63.5	87.5
6	420.0	17.0	89.0	80.5	99.8
7	420.0	14.0	103.0	96.0	102.
8	420.0	17.0	120.0	111.5	97.6
9	420.0	16.0	136.0	128.0	98.7
10	420.0	16.0	152.0	144.0	101.
11	420.0	12.0	164.0	158.0	108.
12	420.0	13.0	177.0	170.5	108.
13	420.0	14.0	191.0	184.0	104.
14	420.0	13.0	204.0	197.5	102.

Regeneration of Diglycolamine Column DGAL2 - DGAR2

Temperature: 52°C

Initial bed concentration: 164 mg/L

Amount of resin: 2.3800 g

Resin bed length: 8.6 cm

Column diameter: 0.84 cm

Average flowrate 1.16 ml/min

Sample Number	Collection Time	Sample Volume	Total Volume	Volume Through	Ligand Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	2100.0	48.0	48.0	24.0	304.
2	2100.0	44.0	92.0	70.0	363.
3	2100.0	50.0	142.0	117.0	311.
4	2100.0	55.0	197.0	169.5	299.
5	2100.0	60.0	257.0	227.0	252.
6	2100.0	66.0	323.0	290.0	216.
7	2100.0	45.0	368.0	345.5	196.
8	2100.0	33.0	401.0	384.5	180.
9	2100.0	34.0	435.0	418.0	196.
10	2100.0	32.0	467.0	451.0	186.
11	2100.0	29.0	496.0	481.5	175.
12	2100.0	27.0	523.0	509.5	177.
13	2100.0	28.0	551.0	537.0	168.
14	2100.0	29.0	580.0	565.5	161.
15	2100.0	33.0	613.0	596.5	
16	2100.0	34.0	647.0	630.0	159.
17	2100.0	35.0	682.0	664.5	152.
18	2100.0	36.0	718.0	700.0	146.
19	2100.0	37.0	755.0	736.5	137.
20	2100.0	40.0	795.0	775.0	132.
21	2100.0	44.0	839.0	817.0	130.
22	2100.0	44.0	883.0	861.0	121.
23	2100.0	44.0	927.0	905.0	
24	2100.0	44.0	971.0	949.0	112.
25	2100.0	<b>44.</b> 0	1015.0	993.0	
26	2100.0	47.0	1062.0	1038.5	105.
27	2100.0	47.0	1109.0	1085.5	
28	2100.0	50.0	1159.0	1134.0	105.
29	2100.0	46.0	1205.0	1182.0	91.5
30	2100.0	37.0	1242.0	1223.5	93.3
31	2100.0	34.0	1276.0	1259.0	91.5
32	2100.0	34.0	1310.0	1293.0	

33	2100.0	34.0	1344.0	1327.0	87.9
34	2100.0	35.0	1379.0	1361.5	
35	2100.0	41.0	1420.0	1399.5	87.9
36	2100.0	45.0	1465.0	1442.5	83.5
37	2100.0	48.0	1513.0	1489.0	74.5
38	2100.0	48.0	1561.0	1537.0	74.5

Regeneration of Diglycolamine Column DGAL3 - DGAR3

Temperature: 62°C

Initial bed concentration: 178 mg/L

Amount of resin: 1.4781 g

Resin bed length: 5.1 cm

Column diameter: 0.84 cm

Average flowrate: 1.66 ml/min

Sample	Collection	Sample	Total	Volume	Ligand
Number	Time	Volume	Volume	Through	Conc.
	(sec)	(ml)	(ml)	(ml)	(mg/L)
1	1260.0	26.0	26.0	13.0	297.
2	1260.0	39.0	65.0	45.5	419.
3	1260.0	31.0	96.0	80.5	387.
4	1260.0	33.0	129.0	112.5	347.
5	1260.0	37.0	166.0	147.5	157.
6	1260.0	47.0	213.0	189.5	130.
7	1260.0	54.0	267.0	240.0	109.
8	1260.0	59.0	326.0	296.5	96.0
9	1260.0	65.0	391.0	358.5	82.6
10	1260.0	29.0	420.0	405.5	82.6
11	1260.0	30.0	450.0	435.0	87.0
12	1260.0	33.0	483.0	466.5	84.4
13	1260.0	36.0	519.0	501.0	87.0
14	1260.0	40.0	559.0	539.0	71.8
15	1260.0	34.0	593.0	576.0	70.0
16	1260.0	24.0	617.0	605.0	69.1
17	1260.0	26.0	643.0	630.0	68.2
18	1260.0	29.0	672.0	657.5	142.
19	1260.0	29.0	701.0	686.5	137.
20	1260.0	31.0	732.0	716.5	124.
21	1260.0	33.0	765.0	748.5	122.
22	1260.0	35.0	800.0	782.5	118.
23	1260.0	36.0	836.0	818.0	105.
24	1260.0	36.0	872.0	854.0	103.
25	1260.0	36.0	908.0	890.0	
26	1260.0	35.0	943.0	925.5	98.7
27	1260.0	44.0	987.0	965.0	
28	1260.0	32.0	1019.0	1003.0	89.7
29	1260.0	31.0	1050.0	1034.5	
30	1260.0	31.0	1081.0	1065.5	87.9
31	1260.0	30.0	1111.0	1096.0	
32	1260 0	30.0	1141 0	1126.0	87.9

33	1260.0	30.0	1171.0	1156.0	
34	1260.0	32.0	1203.0	1187.0	87.0
35	1260.0	33.0	1236.0	1219.5	
36	1260.0	37.0	1273.0	1254.5	75.4
37	1260.0	37.0	1310.0	1291.5	
38	1260.0	38.0	1348.0	1329.0	71.8
39	1260.0	35.0	1383.0	1365.5	
40	1260.0	35.0	1418.0	1400.5	
41	1260.0	34.0	1452.0	1435.0	67.3
42	1260.0	32.0	1484.0	1468.0	
43	1260.0	33.0	1517.0	1500.5	
44	1260.0	33.0	1550.0	1533.5	65.5
45	1260.0	33.0	1583.0	1566.5	
46	1260.0	32.0	1615.0	1599.0	
47	1260.0	33.0	1648.0	1631.5	61.9
48	1260.0	33.0	1681.0	1664.5	
49	1260.0	33.0	1714.0	1697.5	
50	1260.0	34.0	1748.0	1731.0	57.9
51	1260.0	35.0	1783.0	1765.5	
52	1260.0	36.0	1819.0	1801.0	
53	1260.0	35.0	1854.0	1836.5	52.9
54	1260.0	37.0	1891.0	1872.5	75.4
55	1260.0	28.0	1919.0	1905.0	
56	1260.0	41.0	1960.0	1939.5	
57	1260.0	38.0	1998.0	1979.0	48.5
58	1260.0	37.0	2035.0	2016.5	
59	1260.0	35.0	2070.0	2052.5	46.7

Wayne Bernard Bolden was born in Detroit, Michigan on April 15, 1959. After graduating from J.O. Johson High School in Huntsville, Alabama, he enrolled at the University of Tennessee in Knoxville. He received his B.S. degree in Chemical Engineering from that university in June 1982. In the following fall term, he entered the Ph.D. program in Chemical Engineering at Louisiana State University. He is presently a candidate for this doctorate and hopes to complete the requirements for the degree in the fall of 1986.

## <u>VITA</u>

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## DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Wayne Bernard Bolden

Major Field: Chemical Engineering

Title of Dissertation: Amine Removal from Aqueous Process Streams by Ligand Exchange

Approved:

Frank R. E T Professor and Chairman

Dean of the Graduate/School

**EXAMINING COMMITTEE:** 

U W.(

Date of Examination:

November 19, 1986