PRECIPITATION OF PHOSPHATES IN SEWAGE WITH LANTHANUM: AN EXPERIMENTAL AND MODELLING STUDY

PRECIPITATION OF PHOSPHATES IN SEWAGE WITH LANTHANUM: AN EXPERIMENTAL AND MODELLING STUDY

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ABSTRACT

Canada and the United States by the "Great Lakes Water Quality Agreement" have designated that the discharge of phosphates in sewage to the Great Lakes will be controlled. In the majority of cases, chemical precipitation is the treatment method to be used. The selection of the chemical dosage needed is empirical and requires that extensive experimental studies be carried out at each wastewater plant.

The problem of estimating the chemical dosage is approached in this work on a more fundamental basis. The precipitation of phosphates with lanthanum is assumed to be representative of a chemical system at a metastable equilibrium. The dosage which results in the desired aqueous phosphate concentration at this state is estimated with an equilibrium model of the system. This model includes the reactions of major inorganic species found in wastewater.

Lanthanum is an efficient precipitating agent which causes a low residual phosphate concentration to result, even when added in quantities based upon the stoichiometric requirements. Also, lanthanum can be recovered by an economically viable process and recycled.

The solubility products of lanthanum, ortho-, pyro- and tripolyphosphate, lanthanum hydroxide and carbonate and the stability constants of the hydroxide and polyphosphate ion complexes were measured. The experiments were carried out in distilled water at ion concentrations typical of the magnitude to be used in an actual treatment process. With this information, and solving the complex chemical equilibria problem for a set of over fifty separate reactions, it is shown that the extent of precipitation of ortho- and polyphosphates from a municipal wastewater can be accurately predicted. A computer program was written to predict the lanthanum dosage required for a specific residual of dissolved phosphates given the water quality of the wastewater expressed as the total aqueous concentrations of ortho- and polyphosphates, calcium, magnesium, carbonates, sodium, chloride, sulphates and pH.

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I INTRODUCTION

Debate and uncertainty arise as to the role of phosphorus as the nutrient limiting the rate of primary productivity in natural waters, particularly the Great Lakes. However, agreement exists that phosphorus is an important nutrient contributing to the eutrophic state of these waters. Also, among the macro-nutrients of carbon, nitrogen, and phosphorus, only the influx of the last element is feasible to control. This situation occurs principally because of two factors. First, the paths by which phosphorus travels through the lake ecosystem results in this element being concentrated in the bottom sediments under oxic conditions. Also as no aqueous phase for this element occurs naturally, phosphorus is not recycled between atmosphere and lake. Thus, the potential exists for this nutrient to limit primary productivity in the lake. Second, a major portion of the phosphorus influx resulting from man's activities are found in wastewaters. This stream is more convenient to collect and treat as compared to surface runoff or the receiving water itself. These statements are expanded and supported with reference to previous studies in Appendix I, section 1.

Based upon these facts, federal, provincial and state governments in the Great Lakes Basin have responded by designating phosphorus as the principal element to be controlled. This response has taken the form of legislation:

(i) limiting the concentration of phosphorus in wastewaters discharged to the Great Lakes at 1 mg/l or less (for flows greater than 1 MGD),

(ii) limiting or banning the use of phosphorus in detergent formulas,

(iii) providing funds for phosphorus pollution abatement programs (Canada is to spend 250 million dollars till 1975, while the United States 18 billion dollars in the same time period). Further details are provided in Appendix I, section 2.

In almost every case, chemical precipitation has been selected as the treatment method to remove phosphates. Lime, alum and iron salts are the precipitating agents most commonly chosen. This method can be implemented quickly and at slight capital expense as the process is operated simultaneously in existing primary and secondary treatment facilities, (see Appendix I, section 3 and 4).

Problems remain with this process. First, the techniques available to estimate the chemical dosage are empirical and require trials to be carried out at each treatment site. The collection of this data is expensive (in Ontario, six million dollars has been provided for research related to phosphate removal) and is applicable only to wastestreams in their present condition. Second, when chemical precipitation is carried out simultaneously with conventional treatment, additional amounts of biological chemical sludge are produced. The disposal of this sludge increases the cost of treatment by an amount which this writer has calculated to approach the cost of precipitating chemicals themselves, (see Appendix I, section 4). This cost will continue to increase in the future as the number of alternative methods for disposal becomes limited (e.g., as nearby landfill sites become unavailable). Third, with present treatment practices neither phosphates nor the metal salts are cycled either within the process or the marketplace overall. Instead, these methods cause a continuous depletion of these raw materials.

Considerable knowledge exists as to the reactions of phosphates with various cations and anions in water, (see Appendix I, section 10). Also, earlier investigations had shown the reactions of orthophosphate with aluminum, ferric and lanthanum cations to be extremely rapid, (see Appendix I, section 6). A wastewater treated with these precipitants can be expected to quickly reach a metastable equilibrium. Therefore, it appears feasible to depict this treatment process as a set of chemical reactions at equilibrium. Each reaction occurring in this system can be represented by a nonlinear equation. By solving the set of equations simultaneously, the concentrations of components (e.g., phosphates) in a treated effluent can be predicted. The effects of the chemical dosage and certain inorganic compounds commonly found in wastewaters can be determined by solving these equations under various initial conditions. Thus, a mathematical model can be used as an alternative to the empirical tests that are now carried out to determine the effect of chemical dosage upon a particular wastewater.

Such models have been proposed to describe the distribution of soluble components found in seawater, lakes, groundwater, and in sewage treatment plant streams when these aqueous systems are in contact with certain solid phases (see Appendix I, section 8). The structure of an equilibrium model is flexible. New or different components in wastewater not originally considered can be added simply. Similarily much of the data for the model is kept when one precipitating cation is substituted for another.

A computational scheme is required to solve the model's equations. The software package known as "CHEMIST" developed by Rand Corporation was used to carry out the equilibrium calculations. The solution approach is based upon finding those concentrations of the aqueous species which minimize the Gibbs Free Energy of the system. This computer program was selected because first the set of solid phases which exist at equilibrium is not required to be known a priori, only a set of possible phases. Second, partial derivatives are calculated by this program. A review of the generalized computer programs available in the literature is presented in section 9 of Appendix I.

Lanthanum was chosen as the precipitant because of its chemical properties. The nature of this cation is such that the bonds formed in soluble complexes are principally ionic, and its size results in a reduced probability for such complexes to exist, (see Appendix I, section 5). In comparison, aluminum and iron form a number of complexes, particularily with the hydroxide ion, which have yet to be thoroughly characterized. The reduced tendency to form complexes accounts in part for the efficiency of lanthanum as a phosphate precipitant. As discussed in Appendix I, section 6, lanthanum has been shown to remove more phosphate over a broader pH range than either aluminum, ferrous or ferric cations when compared on a molar basis. The cost of lanthanum salts requires that the cation be recovered. Of the processes investigated by myself and others, the most feasible one is the treatment of lanthanum phosphate precipitates with a strong alkali. A lanthanum hydroxide precipitate and an alkaline solution of sodium phosphates results. The lanthanum sludge is separated and then redissolved in an acid. The soluble lanthanum salt can now be reused. The sodium phosphates can be precipitated with calcium to form "phosphate rock"; a raw material used in the manufacture of polyphosphate compounds. The operating cost of the recovery scheme has been estimated at approximately 7¢/1000 gallons of incoming sewage treated, (see Appendix I, section 7). In comparison, the disposal cost of the additional biological-chemical sludge produced when precipitants are added directly to existing treatment facilities is 4 to 5¢/1000 gallons (see Appendix I, section 4).

At present, lanthanum itself has few commercial uses, and is usually a byproduct of extraction methods aimed at concentrating more valuable elements such as thorium, (see Appendix I, section 5).

The objective of this work is to develop a computer model which will predict the lanthanum dosage required to achieve a specified residual phosphorus concentration. The model is based upon the observation that the treated wastewater quickly approaches a metastable condition with the precipitates. The model considers not only the reactions of the lanthanum cation with the ortho- and polyphosphate anions but also the reactions of these components with calcium, magnesium carbonates, sodium, chloride, sulphate, hydrogen and hydroxide ions. These compounds are assumed to represent the principal inorganic components found in sewage. With the phosphates, their initial concentrations are specified as a condition to the numerical solution. Altogether, the formation of fifty-two species is simulated in the aqueous solution. This phase is assumed to be in equilibrium with carbon dioxide at atmospheric conditions (i.e. $pCO_2 = 3 \times 10^{-4}$ atm) and any or all of the following precipitates:

(i) lanthanum phosphates (ortho-, pyro-, and tripoly-)
(ii) lanthanum hydroxide
(iii) lanthanum carbonate
(iv) calcium hydroxyapatite
(v) magnesium calcium carbonate

The model is constructed from information previously published and supplemented with data obtained from experiments. Specifically, from these experiments, solubility parameters were estimated for lanthanum, ortho-, pyro-, and tripolyphosphate, hydroxide and carbonate plus stability parameters for soluble lanthanum polyphosphate and hydroxide.

These parameters are measured at experimental conditions similar to the actual treatment situation. Though the model has the same format that is normally used to describe a chemical system at equilibrium, its parameters have been measured in a manner which permits the prediction of the wastewater composition immediately after chemical treatment and precipitation (i.e. at a metastable condition). Thus the parameters are not true equilibrium constants.

The model's predictions are verified by comparison to observations made on samples of raw sewage which have been treated with lanthanum. This model predicts the minimum residual phosphate concentration which can be achieved for a given chemical dosage. An increase in the phosphate concentration and hence decrease in removal efficiency may be observed in the full scale treatment process, because of the effectiveness at which precipitates are removed. Estimates of the efficiency of solids separation are not within the scope of this model.

II COMPLEX CHEMICAL EQUILIBRIA

The computational scheme is the important component of the equilibrium model. This scheme needs a general format which can depict the many different chemical species in a system with a set of algebraic terms and the reactions among these species as a set of mathematical equations. Also, efficient methods which solve these equations yield estimates of the species' concentrations when the system is at equilibrium. The software package called "CHEMIST" which is made up of thirty-five subroutines meets these requirements. The programs were developed by the Rand Corporation with support from the United States Air Force under Project "Rand" (Contract no. F44620-67-C-0045). In this chapter, the scheme's principles of operation along with modifications made for this work are reviewed. Further details are provided in Appendix II.

II.1 An Algebraic Description of the Chemical System

The parameters defined here are a part of "CHEMIST's" notation plan and are used with the same meaning throughout this text. All chemical compounds in the system are called "species". Within this group, a subset of species exists with which all other species can be formed from linear combinations of the elements of this subset. These elements are called "components". The linear combinations of components represent the reactions which yield the various species. For example, the formation of the species, "H_3PO_4" results from the addition of the components "H+" and "PO_4-3" written as:

$$H_3PO_4 = 3H^+ + PO_4^{-3} \qquad (1)$$

where the constants before each component are the stoichiometric coefficients. In a general notation, where species are identified as X_i, components B_ℓ, and the stoichiometric coefficients "$a_{\ell i}$", every reaction takes on the form:

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$$X_i = \sum_{\ell=1}^{M} a_{\ell i} B_\ell \qquad (2)$$

where M is the total number of components.

The stoichiometric coefficients can assume positive, negative or zero values. The latter value indicating the component "ℓ" is not a part of species "i". The arrays of stoichiometric coefficients can be conveniently stored as a matrix. The columns of this matrix represent the molecular formula for each species with respect to its components. The matrix's dimensions are M x N, where the symbols refer to the total number of components and species respectively. An example of the construction of this matrix for an aqueous Calcium-Phosphorus -Carbonate System is illustrated in section 1 of Appendix II.

In a real system, the group of chemical compounds coexisting in a homogeneous medium is called a phase. In "CHEMIST" notation, the corresponding group of species is called a compartment. All compartments, species, and components are identified by numbers and alphanumeric names.

The total mass (i.e., the sum of the moles of each component and the free energy parameters or equilibrium constants associated with each species are the independent variables of the chemical equilibrium problem. The number of moles of the principal aqueous components, (i.e. the hydrogen and hydroxyl ions), are chosen such that the mass of water formed at equilibrium occupies 1 liter. The dependent variables are the number of moles of each species present at equilibrium. In order to solve the problem, the following is required:

(i) identification of all components, species and compartments

(ii) matrix of stoichiometric coefficients,

(iii) total number of moles of each component,

(iv) free energy parameter of each species or the equilibrium constant for its formation reaction.

Tha manner in which this information is introduced into the computer program is also illustrated in section 1, Appendix II.

The temperature and pressure of the system at equilibrium are also independent variables, but are specified indirectly by the values of the free energy parameters of equilibrium constants.

A note concerning the physical dimensions of the program. At its present dimensions, "CHEMIST" is capable of accepting 160 species formed from a maximum of 60 components. A total of 460 coefficients may be used to describe the reaction stoichiometry of these components. The species may be distributed among 25 compartments with the restriction that total number of compartments and components not exceed 75. The computer storage required to accommodate these dimensions and the 35 subroutines is slightly less than 100,000 words on the Control Data Corporation model 6400 computer.

II.2 Mathematical Statement of Chemical Equilibria

The concentration of species can be expressed on the molal, molar, or mole fraction scales. The molar scale is used because of two advantages:

(i) less input information is required (e.g., no density information),

(ii) mole fraction scale approaches the activity of a species to a closer extent in dilute solution than either the molar or molal scale (D-9).

Using the same notation as before, X_i represents the number of moles of species "i" and $\overline{X}_k$ the total number of moles in compartment "k". The mole fraction "$\hat{X}$" of species "i" is given by:

$$\hat{X}_i = X_i/\overline{X}_k \qquad (3)$$

The concentrations of species at equilibrium are defined by either the mass action laws or the free energy function formulated by Gibbs and others (G-4). In the first approach, the equilibrium concentration of species "i" is given by:

$$\hat{X}_i/\overset{M}{\underset{\ell=1}{\pi}} \hat{X}_\ell^{\,a_{\ell i}} = K_i \qquad (4)$$

where (i) K_i is the equilibrium constant

(ii) $\hat{X}_\ell$ is the equilibrium concentration of the component "ℓ".

A set of these nonlinear expressions must be solved simultaneously to determine the equilibrium state. In the second approach, the equilibrium concentrations of the species are defined as those which minimize the total free energy of the system. Gibbs has shown that this minimization is equivalent to satisfying the mass action laws. The latter approach is used in "CHEMIST" where the problem of estimating the species concentrations becomes the general problem of optimizing a multivariable function.

Now consider the form of this function. The free energy of each species as a function of that species' concentration is given by the Lewis and Randall relationship which states:

$$F_i = X_i(C_i + RT \ln \hat{X}_i) \tag{5}$$

where.
(i) F_i is the Gibbs free energy of species i,
(ii) C_i is the free energy parameter of species i,
(iii) R is the universal gas constant,
(iv) T is the temperature of the system in degrees Kelvin.

The total free energy of the system is the sum of all species in all compartments or:

$$F \text{ system} = \sum_{i=1}^{M} F_i \tag{6}$$

Shapiro and Shapley (S-4) have shown that the minimization of equation (6) results in a gobal minimum when the system is ideal, (i.e., the concentration of a species is equivalent to its activity). –

The values of concentration which satisfy either the mass action laws or free energy functions must also satisfy two sets of constraints to represent a true solution. The concentration of a species must always be positive. In the computer program, this constraint is modified to a condition that the number of moles of any species must be equal or exceed a minimum value, "X_{MIN}", (normally set at 10^{-24} moles). This upgrading of the limit prevents a pathological condition in the numerical solution.

The species' concentrations at equilibrium must also satisfy the mass balance equations which are a statement of the conservation of matter. In the general notation, the M linear equations (one for each component) are represented as:

$$\sum_{i=1}^{N} X_i \, a_{\ell i} = B_\ell \qquad (7)$$

for $\ell = 1,2,\ldots M$

An extra component, the total charge in the system, can also be considered. Normally, this takes on the value of zero. If the elements $a_{\ell i}$ represent the positive or negative charge of each species "i" then equation (7) can be used to represent a charge as well as a mass balance.

This set of linear constraints are added to the free energy function with the use of the Lagrange multipliers, "Π". The expression to be minimized now becomes:

$$F \text{ system} = \sum_{i=1}^{N} X_i (C_i + RT \ln \hat{X}_i) - \sum_{\ell=1}^{M} \Pi_\ell \left(\sum_{i=1}^{N} a_{\ell i} X_i - B_\ell \right) \qquad (8)$$

The number of unknowns to be found has increased from the set of N values of X (i.e., the moles number of the species) to now include the set of M values of Π (i.e., the Lagrange multipliers). The numerical techniques employed to obtain a solution becomes the topic of the next section.

A final note concerning the free energy parameter C_i. Normally this parameter represents the free energy per mole of species "i" in its standard state (i.e., a condition of specified temperature and pressure and unit activity of species "i"). This definition of the parameter is inconvenient as the equilibrium constant rather than the free energy values of species are normally reported in the literature. Fortunately by multiplying equation (8) by factor 1/RT and setting the free energy parameters of the components to zero, the parameters of the remaining species are equal to $\ell n\ K_i$ (i.e., the equilibrium constant for the formation reaction of species "i"). The rationale of this transformation is provided in section 1 of Appendix II. While the division of equation (8) by a constant reduces the value of the free energy of the system, it does not alter the location of its minimum value with respect to the mole numbers of the species (S-4).

II.3 The Numerical Solution to the Chemical Equilibrium Problem

Before reviewing the numerical techniques used to solve equation (8), the following properties of the solution need to be defined. A feasible solution is one in which the set of mole numbers "X_i" satisfy the mass balance equations and are nonnegative. If the elements to this set are also nonzero, the solution is further defined as being positive feasible. If no element of this set of mole numbers is arbitrarily large, then the solution is defined as being bound feasible. An optimal solution is one in which the set of mole numbers yields a feasible solution with respect to the mass balance and a minimum value with respect to the free energy expression. Should any element of this set be zero, then the solution is called a degenerant problem. If all elements are positive (i.e., positive feasible solutions with respect to the mass balance equations), then the solution is termed nondegenerate. Shapiro and Shapley (S-4) show (theorem 12.1) that a nondegenerant problem has exactly one optimal solution in an ideal system (i.e., activity of a species is equal to its concentration).

The numerical solution to this complex chemical equilibrium problem is solved in a two-step approach. First, a linear technique is used to find the set of mole numbers "X_i" which yield a feasible solution. Then this set is used as a basis to find an optimal solution.

If a prior estimate, of the mole numbers is available, the projection method is called from subroutine "SOLVE" to calculate a feasible solution. The objective is to find mole number estimates which yield a set of minimum errors (one per species) in the mass balance constraints (equation (7)). This is achieved by the use of Langrange multipliers. An objective function which is the sum of the products of each error squared times a weighting factor is minimized subject to the linear constraints represented by the mass balance equations. A more detailed summary of this method is provided in Appendix II, section 2.

If an initial estimate of the mole numbers is not given, then the linear programming method is used. The solution technique was developed by Dantzig (D-4) and is summarized in Appendix II, section 3. Three problems are solved consecutively to obtain estimates of the mole numbers which yield a feasible solution. First, a linear programming problem is set up to test if the chemical equilibrium problem is degenerate. This condition usually results from an error in defining the chemical system. Second, the free energy function (equation (5)) is linearized by assuming the logarithmic activity terms to be negligible and solving the approximate free energy expression by the linear programming methods. The last problem is resolved for a number of iterations equal to the number of compartments present in the chemical system. All of the problems are solved under the constraints of the mass balance. The solution is calculated by two subroutines, "LP" which manipulates the data into a generalized form, and "SIMPLE" which solves the general linear programming problem.

A two step procedure is used to find the optimal solution from the initial mole number estimates which yield feasible solutions. These steps are called the "First Order" and "Second Order" Methods respectively.

When the partial derivatives of the total free energy of the system are taken with respect to the mole numbers "X_i" in equation (8) and set to zero, a set of exponential functions which define the mole numbers for an optimal solution results. The general form of an equation from this set for species "i" is:

$$\ell n\ X_i = \{\Pi_{\ell=1}^{M} \Pi_\ell\ a_{\ell i} - C_i - 1\} \qquad (9)$$

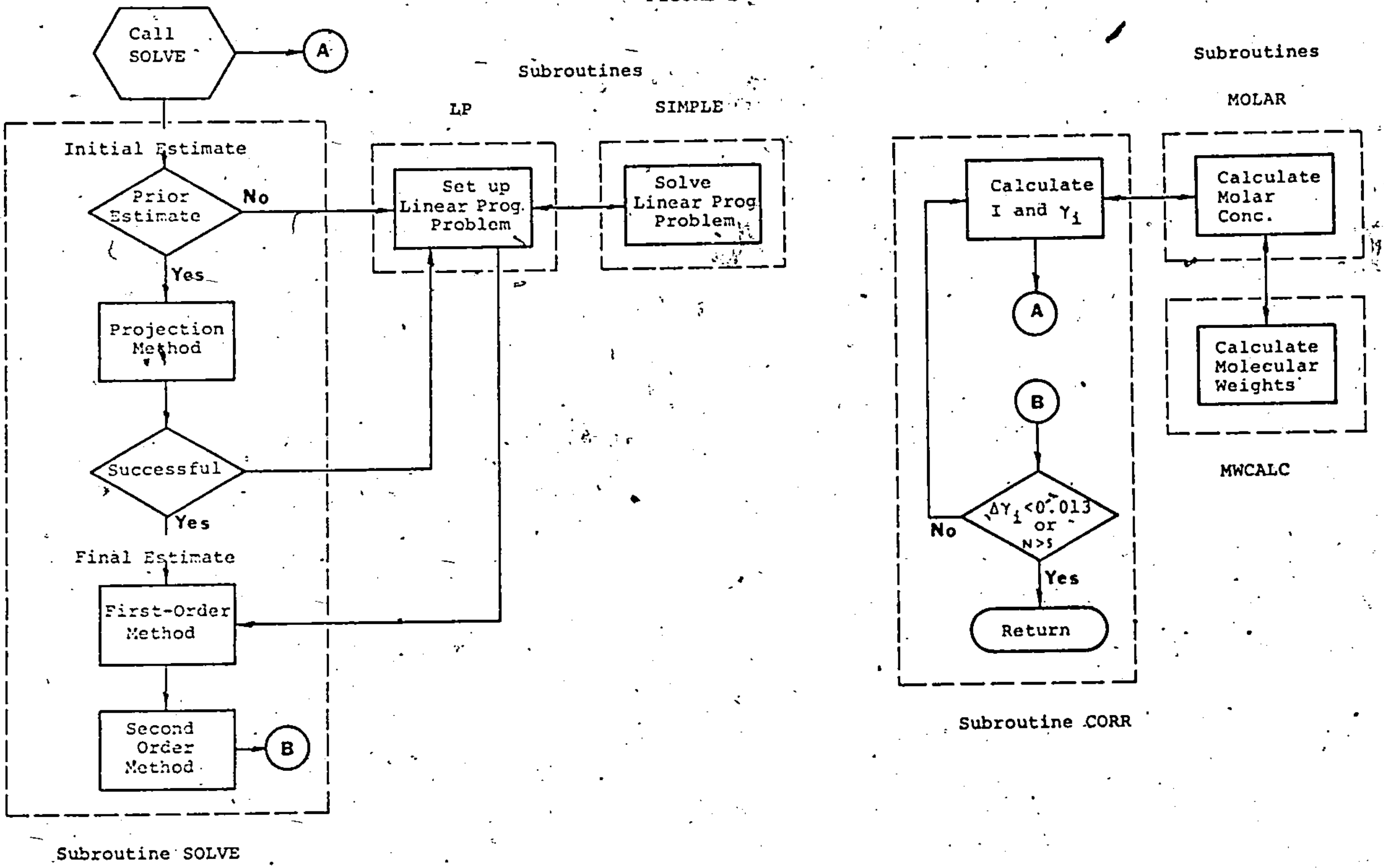
This expression is linearized by substitution of the first order terms of a Taylor series representing the logarithmic term. The truncated series is constructed from prior estimates of "X_i". The linearized set of equations are then solved simultaneously in the first stage to provide new estimates of the mole numbers. The method is stopped when either the change in mole number estimates between iterations is less than a preset tolerance level or the solution is moving away from the optimal value as indicated by a directional derivative. If these tests fail, then an increment is added to the new estimates which now become the prior estimates for the next iteration. The increment is calculated from the product of the difference in mole numbers between iterations and a variable stepsize factor. The factor promotes convergence.

The final estimates from the first stage become the initial estimates in the second. In this stage, improved estimates of the Lagrange multipliers are sought at each iteration, and then used to calculate the mole numbers directly from nonlinear expressions (i.e., equation (9)). The method's success is determined by the errors which these mole number estimates generate in the mass balance constraints (i.e., equation (7)). The method is terminated when the mass balance errors become negligible, the change in multiplier estimates between iterations becomes negligible, or the number of iterations exceeds a limit. The "First" and "Second Order" methods are described in greater detail in Appendix II, section 5 and 6 respectively and by Clasen (C-3).

In summary, the interaction between different numerical techniques can best be seen from the algorithm shown in Figure 1. The solution process is initiated by a call to the subroutine "SOLVE". If a prior estimate of the set of mole numbers is known, then the solution proceeds to the projection method. If no estimte is available, then the subroutine "LP" is called to arrange the data for the linear programming problem. This problem is solved by the subroutine "SIMPLE". If the projection method should fail, then the linear programming subroutine is also called. After this first stage, the estimate of mole numbers represents a positive feasible solution. The next stage is to obtain an optimal solution. This is done by use of the first order and second order numerical techniques located in subroutine "SOLVE". The algorithm shows how

ALGORITHM FOR CHEMICAL EQUILIBRIUM CALCULATIONS

FIGURE 1



corrections for ionic activity are made within the solution path. This now becomes the topic for the next section.

II.4 Activity Coefficients

The need for activity coefficients arises from the interaction of the various species within a system, and the effect that this interaction has upon the relationships defining both the free energy of a species and the free energy of the whole system. An ideal solution may be defined as one in which free energy of a species is a function of the temperature and pressure (with respect to the free energy constant) and to the concentration of the species itself. That is, the mole fraction of a species defines its activity as indicated in equation (5). In a nonideal solution, the free energy and, hence, the activity is dependent directly upon not only the species concentration itself, but also the concentration of the other species in that phase. This interdependence is often expressed by the product of the species concentration and an activity coefficient. The latter term is a function of all of the other species' concentrations within that phase which exert an influence. This may be represented as:

$$a_i = \gamma_i \hat{X}_i \qquad (10)$$

where "a_i" is the activity, "γ_i" is the activity coefficient, and "$\hat{X}_i$" is the mole fraction of the species "i".

By knowing the activity coefficient, the relationships proposed for describing free energy of ideal solutions can be applied to the nonideal situation.

The circumstances for which activity coefficients need be defined in this work are considered. The systems studied were multiphase, that is, gas, solid and liquid. In the gas phase only one component, carbon dioxide, was considered; and its concentration was assumed to be constant (i.e., the capacity of this phase is assumed infinite). Since its concentration does not change, neither will its activity and; therefore, no coefficient is required in this case. In the solid phases only one species is assumed to exist per phase. No solid solutions were assumed to have formed. Therefore, the mole fraction, and the activity, is always one. * The aqueous phase can be divided into three groups of species. They are:

(i) charged ion components,

(ii) charged species resulting from the combination of ion components,

(iii). uncharged molecules, that is, species arising from the combination of ion components and/or solvent molecule water.

The following convention, as proposed by Denbigh (D-9), was chosen to express the activity of the solute and solvent species. For species other than water, "infinite dilution scale" is most convenient as the fraction of these species

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* Note: For the case in which calcium and magnesium precipitate as a mixed carbonate, a constant stoichiometry is assumed for the ratio of cations to carbonate

cannot be varied to unity without a change of phase. With respect to the solvent, the mole fraction of water is frequently greater than 0.999 in this work; and therefore, its activity is assumed equal to its mole fraction. The interaction between uncharged molecules other than water is believed to result from the Van der Waal's forces. Denbigh (D-9) states that from London's theory a deviation from ideality of approximately 1 percent occurs for solutions in which the mole fraction approaches 0.001. In this work, solutes are considered at the millimole level which places their concentration below this limit. Thus for uncharged species, the activity is assumed equal to the mole fraction. This leaves only the activity of charged species and ion components in aqueous solution to be considered. Denbigh (D-9) states that the forces acting between ions is due to large coulombic rather than Van der Waal's forces. This statement is based upon the fact that the potential energy of interaction varies as to the inverse of the first rather than the sixth power of separation between attracting centers. Thus, one can expect the activity coefficients to differ appreciably from unity even in dilute solutions and that this deviation is strongly dependent upon the ion charge.

In this work, it has been assumed that the activity of a species is influenced by two different phenomena. The concentration of a free ion in solution is decreased when it combines with another of opposite charge to form an "ion complex" or "ion pair". Here the ion pair is considered to be a new product whose formation can be described by the appropriate reaction and equilibrium constant. Thus, the concentration of a free ion estimated here is its actual concentation. The activity of a species is also influenced by the electrostatic forces between ions. This activity is represented as the product of the free ion concentration and its activity coefficient. The concept of segregating these two influences was first put forth by Bjerrum (D-5). In simple electrolytes (i.e., solutions of 1 solute) both the influence of ion association and coulombic forces are sometimes combined into a single parameter called the "stoichiometric activity" coefficient. Here, coefficients refer to the ion activity only.

The empirical expression formulated by Davies (D-5) (see Table 29, section 7 of Appendix II) was selected to calculate ion activity coefficients. For an aqueous system at 25°C, the ionic strength is the only independent variable needed for this expression. This variable is calculated from the species' charge and concentration. Because the Davies equation is based upon the molar concentration scale, a conversion factor is needed. This factor is derived in section 7 of Appendix II, and also by Denbigh (D-9).

The "CHEMIST" program was not written to accommodate activity coefficients directly. However for each species the natural logarithm of the activity coefficient may be added to its free energy parameter as shown below. The equilibrium condition is then recalculated with these new set of values.

$$C_i' = C_i + \ln \gamma_i \qquad (11)$$

for i = 1,2,...N

The calculation of the activity coefficients and modification of the free energy parameters is carried out by subroutine "CORR". This subroutine then combines with the subroutine "SOLVE" to calculate the system composition at equilibrium with the corrections made for species' activities. The procedure is to first determine the equilibrium concentration without activity corrections. Then, these concentrations are used to calculate the ionic strength and from this variable the activity coefficients. The free energy parameters are modified according to equation (11) and the equilibrium composition re-estimated with these values by the subroutine "SOLVE". This process is repeated until either the maximum change in activity coefficients between iterations is less than the standard deviation of the estimates from Davies's equation (stated by Davies (D-5) to be 0.013) or an iteration limit is exceeded (usually set at 5). Before returning to the main program, the free energy parameters are reset at their original values.

With the subroutine "CORR" two additional subroutines are required, "MWCALC" and "MOLAR". The first subroutine calculates the charge and molecular weight of each species with this same information given for the components. The latter subroutine calculates the molar concentration of each species in the aqueous solution. For this calculation a solution density is calculated from the equilibrium composition predicted in the last iteration. The density was usually found to change by less than 1 percent from its level in the initial solution.

II.5 Partial Differentiation in the Chemical Equilibrium Problem

The partial derivatives of the dependent variables in the chemical system serve many purposes. These quantities are needed to calculate statistical parameters (e.g., covariance matrix), to carry out a sensitivity analysis, to approximate a new solution when the initial conditions are changed slightly, and to determine initial conditions needed for a particular equilibrium condition. In the last case for example, the partial derivatives are used to determine the total amounts of hydrogen and hydroxide ion which result in a specified final pH level.

The four dependent variables which can be differentiated in the "CHEMIST" program are the mole number and mole fraction of a species, and the total number of moles and pH value of a compartment. In addition, the natural logarithms of these values can also be differentiated. This operation is equivalent to normalizing the variables; thus, the fractional rate of change is determined. The partial derivatives are taken with respect to these independent variables:

(i) number of moles of a component,

(ii) total number of moles of all components needed to form a species,

(iii) a stoichiometric coefficient (i.e., a formula matrix entry),

(iv) the free energy parameter of a species,

(v) a value equivalent to the antilogarithm of a free energy parameter.

The partial derivatives are calculated by the function statements "PART", "CJACOB", and "BJACOB", while "LIST" is a utility subroutine reading and printing information, and "JABY" is a control subroutine directing the calculations. These subprograms are described in section 8 of Appendix II, and by Shapley et al. (S-5).

Often one wants to specify certain conditions at equilibrium, for example the pH value of the aqueous phase. The input format of "CHEMIST" requires for each component that the total number of moles in the system be stated and not its number in one compartment at equilibrium. Thus for a particular pH value, the corresponding total number of moles of hydrogen and hydroxide ion must be known. Because these ions participate in a number of reactions, the initial condition is not easily estimated. This problem is solved by simulating an acid base titration in the chemical system. The change in pH caused by the increase in the number of moles of the acid or base components can be determined by the appropriate partial derivatives. An iterative technique based upon the Newton

Raphson Method and using these derivatives has been programmed in the subroutine "PHSOLVE". This program is described in section 8 of Appendix II.

II.6 A Comparison of Computation Techniques

Midway in this study, results from Morgan and Morel's (M-14) computer program "REDEQL" became available. This computer program solves a chemical equilibrium problem by solving the nonlinear mass actions equations subject to the mass balance constraints. The structure of "REDEQL" is compared to "CHEMIST" in section 9 of Appendix I. The initial quantities of the components and the equilibrium constants, along with the species concentrations at equilibrium are reported for three chemical systems. The first has one aqueous phase, the second an aqueous, gaseous and two solid phases, while in the third two extraneous solid phases are added. These latter two phases are extraneous in the sense that though included in the system, they do not exist at equilibrium. In "REDEQL", a trial and error method is used to select those phases existing at equilibrium, from a set of possible phases, while in "CHEMIST" all species are assumed to exist. In the Rand program the mole numbers calculated for these extraneous phases approaches the zero limit. In Table 1, the model predictions from the third system are compared. From the negligible deviations between the results, it can be concluded that neither method generated a significant round-off error.

during the computations, and that both approaches to selecting those solid phases existing at equilibrium are equally valid.

A further check for computational inaccuracies was made. Cutler et al. (C-5) warn that a round-off error can develop when one species of a phase has a mole fraction in excess of 0.97 and that this phase is much smaller than other phases in the system. In the system simulated here, only the first condition exists, but a further check was made on the possibility of round-off error occurring. A suggested remedy is to make the dominant species (water in aqueous solutions) an input component, and not a product species. This allows the free energy constant of the dominant species to be set to zero. A trial was made for the lanthanum pyrophosphate system containing aqueous and solid phases, in which the components, the hydrogen and hydroxyl ions, were replaced by water and hydrogen ion. The six components and sixteen species for this system are given in Table 36. No difference was found in the equilibrium concentrations calculated with either set of components.

TABLE 1

COMPARISON OF EQUILIBRIUM CALCULATIONS

Phase	Species	Log-Mole	Concentration
		"CHEMIST"	"REDEQL"
Aqueous	H_2O	1.74	
	H^+	- 5.43	- 5.43
	Ca^{2+}	- 2.64	- 2.64
	Fe^{+3}	- 12.99	- 12.99
	PO_4^{-3}	- 10.01	- 10.01
	CO_3^{-2}	- 9.63	- 9.63
	OH^-	- 8.27	- 8.27
	H_2CO_3	- 5.10	- 5.09
	HCO_3^-	- 5.47	- 5.46
	$CaCO_3$	- 10.32	- 10.32
	$CaHCO_3^-$	- 7.12	- 7.12
	HPO_4^{-2}	- 3.65	- 3.64
	$H_2PO_4^{-1}$	- 2.38	- 2.37
	H_3PO_4	- 5.92	- 5.90
	$FeHPO_4^+$	- 10.43	- 10.43
	$CaHPO_4$	- 5.49	- 5.48
	$Fe(OH)_4^-$	- 15.05	- 15.07
	$Fe(OH)_2^+$	- 7.52	- 7.53
	$FeOH^{2+}$	- 9.95	- 9.96
	$CaOH^+$	- 10.00	- 10.00
		(Mole Numbers)	
Apatite	$Ca_5(PO_4)_3OH$	1.54×10^{-3}	Not reported
Ferric Phosphate	$FePO_4$	1×10^{-3}	Not reported
Carbonate	$CaCO_3$	1.07×10^{-25}	(dissolves)
Hydroxide	$Fe(OH)_3$	5.93×10^{-24}	(dissolves)
Carbon Dioxide	CO_2	3.16×10^{-4}atm.	(gas phase)

III PARAMETER ESTIMATION IN THE CHEMICAL EQUILIBRIUM MODEL

It was necessary to estimate the free energy constants for five lanthanum salts and four polyphosphate complexes. These parameters are needed in the chemical equilibrium model which quantitatively describes the precipitation of phosphates from sewage with the cation, lanthanum.

The model has the form of a numerical optimization method contained in the computer program "CHEMIST". The model response is the composition of the chemical system at equilibrium. The set of species' mole numbers, "X_i", from which this response is calculated are those values that cause the total Gibbs free energy of the system (as defined by equation (8)) to be a minimum. For each species, the value of "X_i" which satisfies this condition is defined by equation (9). The model response is determined by solving the set of these equations simultaneously.

From equation (9), it is seen that the mole number is defined by an exponential function of the free energy parameter "C_i" and the sum of the Lagrange multipliers "Π_i". This latter term is in turn a function of the total number of moles specified for each component, "B_ℓ", and the mole numbers of the other species. Thus, the problem of estimating the free energy parameters for certain species is one in which the model response is a nonlinear function of the unknown parameters and independent variables, "B_ℓ".

The estimation of parameters for a nonlinear model is more difficult than a linear one. First, the estimates cannot be found from an analytical solution, but instead from an iterative search method. This method must be efficient with respect to the number of trials in which the model is evaluated. The computer time required to calculate the equilibrium composition for one set of parameter and component values is approximately 0.7 seconds. Second, a criterion is needed to direct the search method. It is hoped that this criterion will yield parameter estimates which are:

(i) unbiased (i.e., the expected value is their true value),

(ii) consistent (i.e., the parameter estimates approach the true values as the sample size increases),

(iii) efficient (i.e., minimum variance is associated with the parameter estimates).

To obtain efficient parameter estimates, experiments are designed (i.e., the levels of the independent variables are selected) on the basis of a criterion which minimizes the variance of these estimates. A sequential approach of designing further experiments is well recommended (D-13). Because the design criterion is a function of the parameters, this approach enables the most recent estimates to be used. Also, the structure or properties of the model can be altered partway in the program, when new insights of the physical system gained from the experimental observations recommend this action.

The final step is to determine the variance associated with the parameter estimates and the effect which this error has upon the magnitude of uncertainty inherent in the model's predictions. The parameter variance is expressed by first knowing or assuming a function which describes the probability distribution of this error and then estimating this function's parameter. The analysis of the propagation of error from the model's parameters to its predictions is carried out on a linearized form of the model in order to simplify calculations. This approximation of the model is usually constructed from a truncated Taylor series.

Himmelblau (H-5) summarizes a number of experiences of parameter estimation in the nonlinear situation. These range from cases in which the model response is calculated from algebraic expressions to situations in which the model response is the numerical integration of either a set of ordinary or partial differential equations. An alternative approach taken is to transform the experimental data in order to simplify the model form. Wilson (W-2) transformed the residence time distribution measured in non-ideally mixed chemical reactors to the frequency domain where it was simulated by an algebraic model for which parameters were estimated.

Blau et al. (B-11) formulated the problem of parameter estimation in chemical equilibrium system on a statistical basis using the principle of maximum likelihood. Blau and his co-workers (B-12, B-13) tested these criteria on two similar models which described the set of polymers formed at equilibrium from either one or two monomers. The set of equilibrium constants and the highest state of aggregation were the unknown parameters needed to predict the average size of aggregates in the polymer system. This average was dependent upon the initial monomer concentration. The nature of the experiments prevented a sequential design to be used. Both the solution of the chemical problem and the parameter estimates were combined into one search technique. The normalized sums of squares calculated from the deviations in the mass balance relationships and the differences between the measured and predicted response were added to form a joint search criterion Parameter estimates which minimized this criterion were taken as a solution to the problem.

III.1 Parameter Estimation

The computer time needed to predict the equilibrium composition at one given set of conditions places a practical limit upon the number of unknown "Ci's" and independent variables. Thus, the reactions between each type of phosphate (i.e., ortho-, pyro-, and tripoly-) and lanthanum were investigated separately. The model of each system had four independent variables or less, and 3 free energy parameters values were unknown. In principle, the technique described here can be extended to any chemical system which can be described by "CHEMIST".

The dependent variables of each chemical system are the total aqueous concentration at equilibrium of two elements (e.g., lanthanum and phosphorus). As the equilibrium model predicts concentrations of individual species, the predicted response is calculated as the sum of concentrations of those species formed from the particular element. These concentration terms are weighted in the summation with respect to the stoichiometric coefficients pertaining to the element.

The equilibrium composition predicted by the model is a function of both the unknown free energy parameters and a second set of parameters which are treated as constants. These parameters generally belong to reactions in which lanthanum and phosphate are not components; for example the association of the hydrogen ion with various anions. This latter set of parameters have been carefully selected from the literature and their values are reported with their reference sources in section 10 of Appendix I.

The two search criteria used here to find parameter estimates are based upon the principle of maximum likelihood as shown in section 1 of Appendix III. Both are formulated for a multiresponse model. The choice of which one to use is contingent upon the investigator's knowledge about the errors associated with each measured response. In the investigation here, information concerning these errors improved as more experiments were carried out.

For the purpose of this discussion, the following general form is used to represent the model and its variables:

$$Y_{iu} = N_i(\mathcal{X}_u, \beta) + \varepsilon_{iu} \qquad (12)$$

where (i) $\mathcal{Y}_u = (Y_{1u}, Y_{2u} \ldots Y_{ku})$ is the vector of k observations (or measure responses) made in the u-th experiment,

(ii) N_i is the model function for the i-th response,

(iii) $\mathcal{X}_u$ is the vector of L independent variables which define the conditions of the u-th experiment,

(iv) β is the vector of p parameters to be estimated,

(v) ε_{iu} is the error associated i-response in the u-th experiment.

In every case, it is assumed that observation errors in each experiment are independent (i.e., $E(\varepsilon_{iw}, \varepsilon_{ju}) = 0$, all i, j, $u \neq w$) and that each error has an expected value of zero (i.e., $E(\varepsilon_{iu}) = 0$).

Box and Draper (B-16) formulated the criterion, labelled "A" here, for the situation in which the observation errors are unknown but are assumed to be constant with respect to each response for all experiments. Estimates of the unknown elements of the vector B are those values which minimize the determinant:

$$\text{Criterion } A = | V_{ij} | \qquad (13)$$

where the elements V_{ij} are cross-products of the residuals or differences between the measured and predicted responses summed over all experiments. That is:

$$V_{ij} = \sum_{u=1}^{N_x} \{Y_{iu} - N_i(\mathcal{X}_u, \beta)\}\{Y_{ju} - N_j(\mathcal{X}_u, \beta)\} \qquad (14)$$

where N_x is the total number of experiments.

In the situation in which estimates of the observation errors are known, the likelihood estimates of the elements of B are those values which minimize criterion B, given by:

$$\text{Criterion B} = \sum_{u=1}^{N} \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma_u^{ij} V_{ij}^u \qquad (15)$$

where σ_u^{ij} is an element of the inverse covariance matrix for the observations and V_{ij}^u the cross product of residuals in the u-th experiment. Because the final summation in criterion B is with respect to the experiments, it is not necessary that the observation errors be constant for each response. The derivation of criterion B is reviewed in section 1 of Appendix III.

In the initial experiments, the values of ϵ_{iu} were unknown, and thus criterion A was used to determine free energy parameters. Further along, estimates were obtained from duplicate experiments. The elements of the covariance matrix of y_u, were calculated with these estimates for the diagonal terms, (i.e., $\sigma_{ii}^u = E(\epsilon_{iu^2})$), while off diagonal elements were set to zero, (i.e., the errors ϵ_{iu} and ϵ_{ju} are assumed not to be correlated for all values of i and j). The elements from the inverse of this covariance matrix were then used in criterion B to evaluate free energy parameters.

After a number of experiments had been completed in duplicate, the errors in the lanthanum, phosphate and carbonate analyses were analyzed. In such case, the error was found to be directly proportional to the measurement itself, (based on at least 17 data points). The ratios of the errors to the measurements approach a normal distribution as shown in

The error estimates were then calculated as the product of the average of these ratios times the observation. Box (B-18) asserted that these prime errors in the actual measured quantities are often uncorrelated because knowledge of the measuring technique shows that the measurements are independent or simply there is no compelling reason to assume otherwise. For the experiments here, each response was measured by a different analytical method, and thus the errors in these measurements are assumed to be uncorrelated. Box went on to define a second class designated as effective errors which account for the effect of both the prime errors and the uncertainty in specifying the levels of the independent variables, X_u, upon the measured response. The effective errors are generally correlated. Estimates made for errors in X_u, assumptions made with respect to the properties of both errors, and the expressions used to combine both into an estimate of the effective errors are reviewed in section 1 of Appendix III. Estimates of the effective errors became the elements of the covariance matrix which was used in turn in criterion B to evaluate parameters. For each chemical system, the transition from one type of parameter estimation criterion to another is noted in the appropriate sections of chapter IV.

Though minimizing the search criteria minimizes the residuals (i.e.,differences between the observed and predicted responses), a further analysis was carried out at each stage after parameters had been evaluated. First, the magnitude of of a correlation was determined by plotting each set of residuals against their predicted response. These plots were drawn by the computer program. As noted by Draper and Smith (D-12), general trends in these plots indicate problems. For example, the model may be an inadequate description of the observations, or the variance of the measured response is not constant. In the experiments performed here, the latter situation occurs. However, the elements of the inverse covariance matrix (i.e., σ_u^{ij}) used in criterion B act as weighting factors to overcome this problem. A disappearance of trends in the residual plots was observed when criterion A was substituted with type B.

An alternative statistic used to judge parameter estimates is the multiple correlation coefficient. The square of this term is defined as the ratio of the variance of the observations which is removed by the model, compared to the variance initially present. These coefficients were calculated for the final parameter estimates in each chemical system and were found to be greater than 0.99 as reported in chapter IV. The expression used to calculate these coefficients is reported in section 1 of Appendix III.

A direct search method was chosen for the nonlinear estimation problem. This approach avoids the need to approximate numerically the partial derivatives of the search criterion with respect to the model parameters. The "Flexible Simplex" algorithm first proposed by Nelder and Mead (N-1) was used here. Box (B-19) from his evaluation of four direct search methods found that the Simplex algorithm was as efficient as the Powell algorithm in cases where three or less parameters were to be estimated. In addition to the "CHEMIST" package, another four computer routines were required to carry out the parameter estimation. These are:

(i) "TST"-the main program directing the input and output of information and the order of computations,

(ii) "SIMPLEX"-the subroutine which directs the search parameters using the Simplex algorithm,

(iii) "OBJECT"-subroutine which calculates the search criterion (i.e., objective function for each estimate),

(iv) "MODEL"-subroutine which transfers the equilibrium composition predicted by "CHEMIST" to the search criterion.

A descriptive algorithm indicating the manner in which these subroutines are linked is provided in section 2 of Appendix III.

III.2 Experimental Design

The objective in designing experiments is to select levels of the independent variables which result in the minimum uncertainty with respect to the parameter estimates. Also, it is hoped that the design is efficient in the sense that this objective is accomplished with the least number of experiments. The final design procedure had evolved through a series of improvements. These were:

(i) increased information concerning the values and properties of the variance-covariance of V_u,

(ii) availability of computer programs with more efficient search algorithms.

In the initial experiments, when the values of the observation errors ε_{iu} were unknown, they were assumed constant for each type of response in all experiments. The criterionused to select levels of the independent variables was a modified form of the criterion suggested by Draper and Hunter (D-13). Values of X_u were chosen which maximize the determinant:

$$D_1 = \left| \sum_{i=1}^{k} \sum_{j=k}^{k} \omega_i^T \omega_j \right| \tag{16}$$

where ω_i is a $(N_x + n_x)$xp matrix whose elements are the partial derivatives of the i-th response of the model N_i with respect to each parameter calculated for all the sets of values of X_u. That is:

$$\{W_i\}_{a,b} = \frac{\partial N_i}{\partial B_b} (X_a, B) \tag{17}$$

The term N_x refers to the number of experiments that have already been carried out, while n_x is the number of experiments that are to be selected. The importance of using the most recent parameter estimates is seen from the criterion above, as the partial derivatives are functions of the parameters.

When the covariance matrix of the responses is known but still assumed constant for all experiments, the summation of the matrices $\omega_i^T \omega_j$ is weighted with respect to the elements of the inverse covariance matrix (i.e., σ^{ij}). The design criterion to be maximized is:

$$D_2 = \left| \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma^{ij} \omega_i^T \omega_j \right| \tag{18}$$

This criterion was used at the stage when estimates of the observation errors were available from previous experiments carried out in duplicate. These errors were assumed to be independent (i.e., $\sigma^{ij} = 0,\ i \neq j$).

The most general criterion applies to situations where the covariance matrix is different for each experiment. The criterion (as formulated by Box (B-18)), to be maximized is:

$$D_3 = \left| \sum_{u=1}^{N_x+n_x} \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma_u^{ij} (\omega_i^u)^T (\omega_j^u) \right| \qquad (19)$$

where ω_i^u now refers to one row of p elements of the derivative matrix previously defined. When it became possible to calculate the effective covariance matrix for each experiment (as discussed in section 1), criterion D_3 was used.

The determinant of D_3 has two useful properties. Its elements are an estimate of the inverse covariance matrix of the parameters. This estimate is approximate in that it applies to a linearized form of the model. This form is derived by substituting the first order terms of a Taylor series for the model itself. The square root of the determinant is inversely proportional to the size of the confidence region of the current estimates in parameter space. Thus by maximizing this criterion, the volume of this region is minimized. This volume can be expected to continually decrease as more observations become available for estimating parameters. The return on information about the parameters which will result from further experiments can be estimated by observing the rate of decrease of the confidence region in the previous experiments. This prediction was made by plotting the size of the confidence region versus the number of experiments performed as shown in Figures 6 and 7 in chapter IV. When the size of the confidence region no longer decreased at an exponential rate, no further experiments were planned.

The final experimental design procedure used the search technique based on Powell's algorithm to select levels of X_u which maximized the criterion D_3. Box (B-19) recommended this algorithm as the most efficient, particularly when the problem contains a large number of variables. In the experimental program here, as three or more experiments were selected at each step, the optimum levels of nine or more variables were sought. A description of this algorithm and a computer program has been written by Himmelblau et al. (H-6). Before this program became available, the Flexible Simplex Algorithm was employed.

In the primary experiments, approximate estimates of the independent variables were found simply from a grid search. A network of possible experiments was defined and the partial derivatives calculated at each point. The combinations of these derivatives which maximized either criterion D_1 or D_2 indicated a set of feasible experiments with which to start the investigation.

Seven computer routines in addition to the "CHEMIST" subroutines are required to design experiments. As before in the parameter estimation problem, the main program "TST" directs the input and output of information and the order of computations. Subroutine "MODEL" transfers the information predicted by "CHEMIST" (e.g., equilibrium concentration, partial derivatives) to the design criterion. The actual search for experiments is directed by subroutine "MINI" which in turn calls upon:

(i) "FUN"-to evaluate the design criterion (i.e., objective function),

(ii) "TEST"-to test convergence,

(iii) "SEARCH"-to evaluate the optimum stepsize in one direction.

"EVDET" is a utility subroutine called by "FUN" to evaluate the determinant in the criterion. An algorithm which illustrates the manner in which these subroutines interact is provided in section 3 of Appendix III.

III.3 Error Estimates

After the experiments for each type of phosphate compound had been completed, an estimate of the covariance matrix for each set of free energy parameters was made. As noted in III.2, the elements of the determinant for the experimental design criterion D_3, (equation (19)), are equivalent to the elements of the inverse parameter covariance matrix. Thus, the terms of the determinant were evaluated for those experiments which had been completed, and then the inverse of this matrix calculated. In order to compare the correlation between the different free energy parameters, the paramtere covariance matrix was normalized by:

(i) dividing the estimates of the parameter variance by itself (i.e., the diagonal elements),

(ii) dividing the covariance estimates (i.e., off-diagonal elements) by the product of the square roots of the two appropriate variance estimates.

The matrix resulting from this operation has a set of values equal to unity along the diagonal, and equal or less than unity off the diagonal. The closer the off-diagonal terms approach unity, the greater the correlation between parameters. For each set of free energy parameters, this normalized matrix is reported in the appropriate section of chapter IV.

The need exists for estimates of the errors associated with the model predictions. The estimates are used to make a meaningful comparison between the model predictions and the observations made from samples of actual and simulated sewage in which lanthanum reacts simultaneously with three phosphate compounds. The error estimates also establish the range in which the total residual phosphorus concentration can be expected to lie when a sample of sewage is treated with an amount of lanthanum specif~~ied by~~ the dosage model.

The errors in the predictions is assumed to be contributed from three sources. These are:

(i) the errors in specifying the levels of the independent variable,

(ii) the errors contributed from the uncertainty in the parameter estimates,

(iii) the errors associated with the actual measurements.

The total variance in the i-th response is estimated as a function of the errors from these three sources by the expression:

$$E(\hat{e}_{iu}^2) = (W_i^u)^T \, \text{Covar}(B) \, W_i^u + (Z_i^u)^T \, \text{Covar}(X_u) \, Z_i^u + E(e_{iu}^2) \tag{20}$$

where (i) W_i^u is a vector of p partial derivatives of the i-th response taken with respect to each model parameter (i.e., free energy constant) considered to be in error,

(ii) Covar(B) is the covariance matrix of the free energy parameters,

(iii) Z_i^u is a vector of ℓ partial derivatives of the i-th response taken with respect to each independent variable whose value is uncertain,

(iv) Covar(X_u) is a diagonal matrix whose elements are estimates of the variance in the independent variables,

(v) $E(e_{iu}^2)$ is the estimated variance in the actual measured quantities.

The sub- or superscript u indicates that the partial derivatives and errors refer to a particular set of independent variables, X_u. This expression is derived upon the assumption that the equilibrium model can be approximated in a local area by a linear form consisting of the first order derivatives of a Taylor series.

For each set of experiments carried out with a phosphate compound, a covariance matrix was calculated along with the free energy parameters (as reported in chapter IV). These three matrices were combined with error estimates reported in the literature (see section 10 of Appendix I) for the free energy parameters of the reactions in which the calcium and magnesium cations associate with the tripoly- and pyrophosphate anions. The resulting covariance matrix, Covar(B), is reported in Appendix V. Covariance was assumed to exist (i.e., the value is not set to zero) only for those parameters which had been estimated together from the same experiments.

As noted before, the independent variables are the numbers of moles of each component, B_ℓ, which are present in the entire chemical system. Among all the components, a subset was chosen where errors in specifying the values of B_ℓ would significantly affect the model predictions. This selection was based upon the relative magnitudes of the partial derivatives of each model response taken with respect to the independent variables. The components and their error estimates are listed in Appendix V. These estimates become the diagonal terms of matrix Covar(X_u). The errors in the independent variables are assumed to be independent to each other, and thus the off-diagonal terms have been set to zero. For the situation in which the observations from experiments are compared to the model predictions, error estimates are based upon experience with the experimental procedures. With the dosage model, the errors specified with values of the independent variables reflect the accuracy with which the chemical components in sewage can be determined with the present analytical methods.

The errors in the actual measured quantities were found from experiments to be fractions of the quantities themselves as shown in section 2 of chapter IV. In the situation where the concentrations of all three phosphate species were measured, the error associated with each concentration is a function of both the error in the determination of the total phosphate concentration and the errors in determining the distribution of phosphate species. An analysis of the propagation of errors from both sources to the final estimate is reviewed in section 7of Appendix IV.

Calculations of the error estimates with equation (20) are carried out in either the main program "TST" or with the dosage model in a subroutine named "EXPER". A listing of this subroutine is included with a listing of the dosage model in Appendix VI . In both cases the values of the partial derivatives are obtained by a call to subroutine "MODEL".

IV EXPERIMENTATION

The experimental studies of the reactions of phosphorus compounds with the lanthanum ion can be divided into three areas. Three phosphorus species were considered, tripoly-, pyro-, and orthophosphate. In the first area, lanthanum was reacted with one phosphorus species in distilled water. This data provided the basis for which to estimate equilibrium parameters for the computer model. Included in this area is a study of the hydrolysis reaction of lanthanum with the hydroxide ion. In the second area, the simultaneous removal of all three phosphate species from distilled water was observed. From this study, the removal efficiency of lanthanum was evaluated, as well as the basis for the comparison of residual phosphorus and lanthanum concentrations observed to those predicted by the equilibrium model. The third area is in the most part similar to the second, the important exception being that wastewater influent from a domestic sewage plant was used as a background solvent. Thus, this data provided a more severe test of the computer model predictions.

The concentrations of the chemical reactants are set at levels which would be on the average observed in domestic sewage. Specifically, this meant that the following levels for the principal reactants:

Phosphate species	1 mM
Lanthanum	1 mM
Carbonates	1 mM - 5 mM
Hydroxide Ion (pH)	6 - 10
Ionic strength "IS"	10 - 50 mM

The lower level of the chemical reactants was determined by the limits of detection of the available analytical techniques. Precipitations, which occur at these low levels of reagents, often result in the formation of an amorphous floc particle, rather than a more well defined crystaline structure. It is realized that the solubility and hence solubility parameters of these amorphous "flocs" are higher than that which constituted the more well defined structure. This is entirely satisfactory. At the wastewater treatment plant, it will be the amorphous flocs which will be formed. It is this phenomenon which the computer model is to simulate.

As indicated in the previous chapter, the order in which experiments were performed and their total number were determined by the experimental design methods. A sequential approach was taken where a set of experiments were designed, parameters estimated, and then the updated estimates used to design further experiments. As noted previously, the number of chemical components (or independent variables) in a chemical system and the number of unknown parameters was constrained in part by the complexity of the computational problem. Restricting each group of experiments to one phosphate species simplified the analysis of the reactions taking place and permitted the evaluation of the removal efficiency for each species. In the following sections, each experimental study is outlined in chronological order from the initial observations to the final parameter estimates. Differences in experimental procedures or analytical techniques are noted when they differ from those outlined in section 6 and 7 of Appendix IV.

IV.1 Study of Lanthanum Hydrolysis

The formation of a soluble complex between the lanthanum and hydroxide ion is expected because of the trivalent charge of the metal ion.

Three previous studies are of interest. Moeller (M-12) in his study, found the presence of only the first complex $LaOH^{2+}$ in a concentration range of 0.4 mM - 10 mM of lanthanum. The solutions were at low ionic strength and consisted of lanthanum sulphate only. Lewis (L-6) investigated the solubility of La_2O_3 as a function of the hydroxide ion concentration in a pH range of 7.5 - 10.5. His results indicated that lanthanum hydroxide solubility in water varies as to the (1.5)th power of the hydroxide ion concentration, instead of the expected third power of dependence. He proposed that the fractional dependence resulted from extensive hydrolysis of the lanthanum ion. Biedermann and Ciavatta (B-9) studied lanthanum hydrolysis in aqueous solutions in which the lanthanum concentration ranged from 0.1 - 1 M with a constant ionic strength background of 3 M perchlorate ion. Both levels are out of the present range of interest. They interpreted the results in terms of three soluble complexes, $LaOH^{2+}$, La_2OH^{5+}, and $La_5(OH)_9{}^{6+}$. Their observations also indicated that the last two complexes formed only as the solution approaches the point of lanthanum hydroxide precipitation.

Moeller had worked in the area of interest with respect to the lanthanum and ionic strength concentrations. It was, however, felt necessary to repeat his experiments as he had used lanthanum sulphate as the rare earth salt. Later studies by Spedding (S-11), had shown the existence of a lanthanum sulphate complex.

The experiments were conducted in the following manner. The rare earth salt used was in a chloride form. Previous work of Spedding (S-12) had shown no chloride complexes below a lanthanum concentration of 0.033 M. Five solutions of lanthanum chloride in the concentration range of 0.4 - 10 mM of lanthanum ion were prepared by dilutions of standardized lanthanum chloride solutions in carbonate free water. The solutions were then brought to a constant temperature of 25°C. The solution pH is then determined by a glass electrode. The final hydrogen ion concentration (as pH) is plotted versus the logarithmetic value of the total lanthanum concentration.

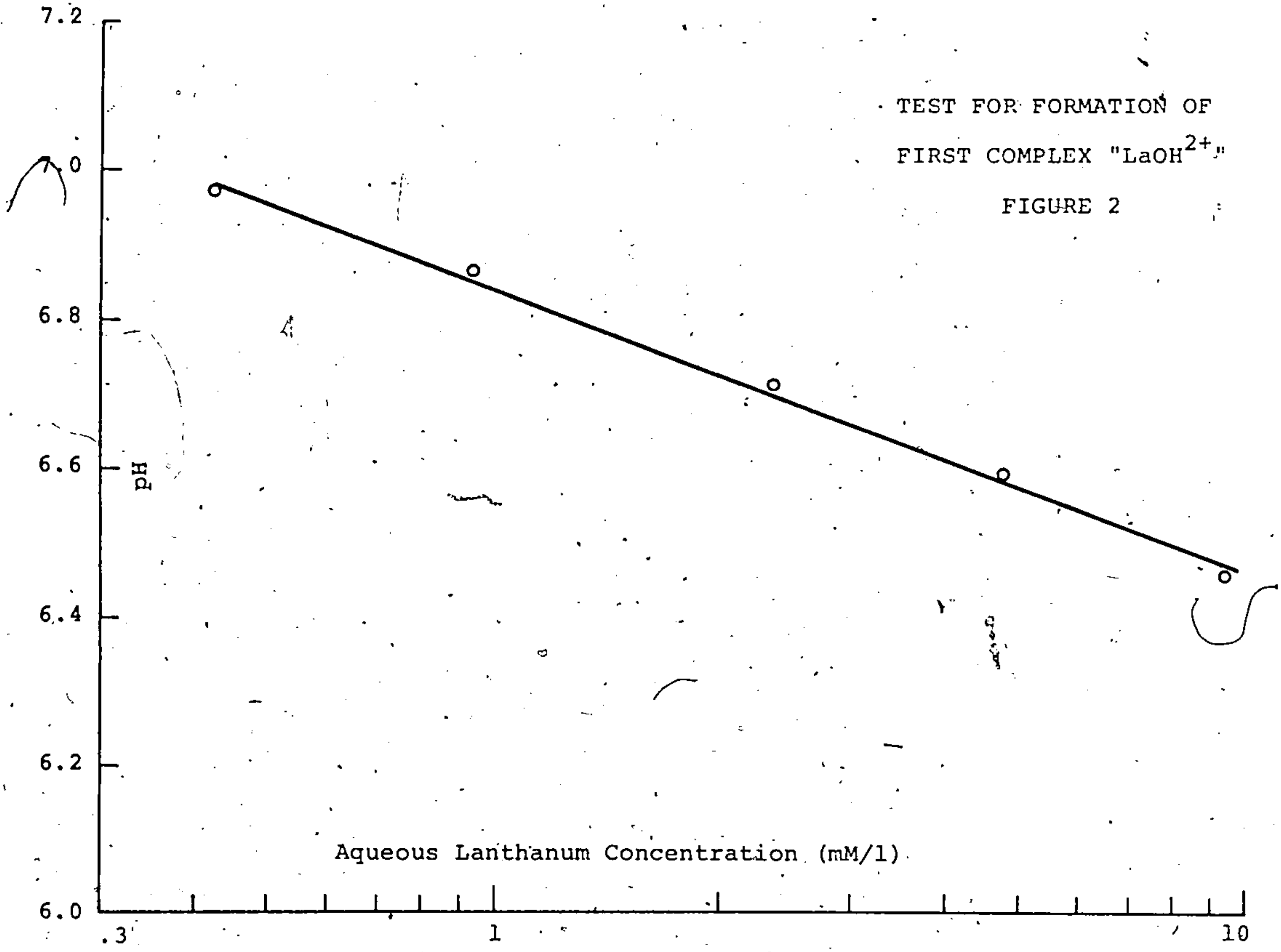
It can be shown from the mass action, and mass balance relationships that if only one simple complex $LaOH^{2+}$ exists, then the above mentioned plot is rectilinear. Figure 2 indicates the existence of only one complex. Using the Davies relationship, which relates the ionic strength of a solution to the individual ion activity coefficients, an expression was derived to relate the measured equilibrium constant to the true thermodynamic value and ionic strength. This function was linearized by a log transformation. The equilibrium constants, as measured from the solution pH value and total lanthanum concentration, were plotted versus the ionic strength to estimate the thermodynamic value.

Table 2 shows a comparison of the estimated stability constant for the lanthanum hydrolysis in comparison to previous studies.

TABLE 2

FIRST STABILITY CONSTANT OF LANTHANUM HYDROLYSIS

	Moeller	Biedermann (B-8)	Present Work
Ionic Strength	Varied	3.0 M ClO_3^-	Extrapolated to zero
pK			



TEST FOR FORMATION OF
FIRST COMPLEX "$LaOH^{2+}$"

FIGURE 2

IV.2 Orthophosphate - Carbonate - Hydroxide Solubility

Four previous studies of lanthanum orthophosphate solubility are of interest. Tannahaev and Vasil'eva (T-1) estimated an approximate solubility product for lanthanum orthophosphate in a solution of ionic strength equal to 0.5 M as the perchlorate ion. Their approximate value was, pKsp = 22.4. Recht and Ghassemi (R-2) investigated lanthanum orthophosphate solubility at the millimole levels expected in a treatment operation. Unfortunately, the residual phosphate levels were below the detection limit of their analysis in the pH range of interest for wastewater treatment. Baxter (B-6), in his studies of orthophosphate precipitation found the normal salt always to be formed and no evidence of a soluble phosphate complex. Matejevic and Milic (M-2) performed a tyndallometric study of lanthanum orthophosphate solubility. They observed slight pH dependence of the phosphate solubility in the pH range of 7 - 9. Also, they found no evidence of a lanthanum orthophosphate complex when an excess of lanthanum ions are present. Rao (R-1) investigated the possibility of lanthanum orthophosphate complexes. He found one, $LaH_2PO_4^{-2}$ to exist at a pH level much below the area of interest in the treatment process.

Based upon these observations, it was assumed that no lanthanum orthophosphate complex is present in the solutions of interest here. Thus, this species is not included in the model. Also because of the difficulties experienced by competing with orthophosphate for lanthanum was needed. This competition would result in a phosphate residual concentration that could be measured with the analytical methods used here. Carbonate was chosen as the anion in competition.

Only one previous study of lanthanum carbonate solubility in the concentration range of interest was found. Jordanov and Havezov (J-3) measured the activity product of lanthanum carbonate. They reported the product for $La_2(CO_3)_3$ to be in the order of 4×10^{-34} at zero ionic strength. This value is reported for a precipitate that has aged 24 hours. They found no evidence of lanthanum carbonate complex at the 1 mM level of total carbonate in solution. Based on this observation, a soluble lanthanum carbonate complex was not considered in the equilibrium model. The solubility of lanthanum hydroxide has been investigated extensively in Soviet Russia. A range of initial lanthanum concentrations, ionic strength, temperature and precipitate age had been considered. From the work of Buchenka et. al. (B-23), Kavalendo et al. (K-1), Ziv and Shectakova (Z-2), Orkanovic et al (O-2), and Mironov et al. (M-10), it was concluded that the solubility product of fresh lanthanum hydroxide precipitate could lie in the range from 10^{-20} to 10^{-23} in a temperature range of 20 - 25°C.

Initially, the model of the chemical system was composed of one aqueous and two solid phases, lanthanum phosphate and lanthanum carbonate. A third phase, lanthanum hydroxide was added at a later point in the experiments. The species, components, their reactions and those free energy parameters assumed to remain constant are reported in Table 32 of Section 1, Appendix IV. The independent variables in this model were the initial concentrations of the components lanthanum, orthophosphate, carbonate and hydroxide ions. A constraint was placed upon the values assigned to the last variable. Test solutions were maintained at basic conditions to prevent the transfer of carbonates as carbon dioxide to the atmosphere. The experimental solutions were prepared from additions of the following stock solutions to distilled water. The solutions were:

(i) lanthanum chloride,
(ii) potassium dihydrogen phosphate,
(iii) sodium bicarbonate,
(iv) sodium hydroxide,
(v) hydrogen chloride.

Additions were always made in order of the decreasing alkalinity in order to prevent the solution from becoming acidic.

The measured quantities were the final concentrations of phosphate and carbonates in solution. At a later stage the lanthanum concentration was also measured. However, in certain experiments the aqueous lanthanum concentration was below the detection limit of the analytical technique. Therefore only information from the first two measurements was used to estimate free energy parameters.

The experimental study progressed from a set of preliminary experiments whose purpose was to test the solubility products reported in the literature; to sets of experiments designed and carried out sequentially. The purpose of these latter experiments was to improve upon the free energy parameter estimates.

For the first twelve experiments, the initial lanthanum and phosphate concentrations were set at levels of 0.25, 0.5, 0.75 and 1 mM/litre; but not at equal concentrations in the same experiment. The carbonate concentration was kept constant at 3 mM/l as well as the solution pH at approximately 8.5. A preliminary analysis performed with the computer had indicated the first two variables to be the more sensitive of the four, hence their values were changed. The initial and final concentrations measured for these experiments are reported in Table 33 of section 1, Appendix IV. Details concerning the experimental procedure and analytical techniques are reviewed in section 6 and 7 of Appendix IV.

Parameter estimates were calculated from the information obtained in these experiments. Because the errors in the dependent variables were unknown, criterion A (equation (13)) was used to calculate the estimates. These values, as shown in Table 3, are higher than the values previously reported in the literature. This indicates that the precipitates formed here are more soluble than had been observed previously. This condition may be due in part to the fragile floc structure which these precipitates had. Additional experiments were designed to improve upon the parameter estimates.

It was convenient experimentally to carryout six experiments at a time. However, the computer time needed by the Simplex algorithm dictated that it would be practical to design only three experiments, (i.e., simultaneously select the levels of twelve variables). Thus, two sets of three experiments were designed. Approximate estimates of the errors associated with the phosphate and carbonate analyses were obtained by repeating these measurements on six different samples. These estimates were assumed to remain constant for all analyses. These error estimates, the free energy parameters, and the partial derivatives evaluated for the first twelve experiments were substituted in the design criterion D_2 (equation (18)). With this criterion programmed as the objective function, the Simplex algorithm was used to design the new experiments. The starting co-ordinates for the search were determined beforehand from a grid search.

A grid was constructed to represent the forty-eight experiments which arise from all of the possible combinations of:

(i) four initial lanthanum concentrations from 0.25 to 1 mM/l in 0.25 mM/l increments,

(ii) same four initial phosphate concentrations;

(iii) three initial carbonate concentrations at 1, 3 and 5 mM/l.

The solution pH was set at 8.5 for all experiments. For each experiment the partial derivatives of the two model responses with respect to the parameters were calculated. The design criterion D_2 (equation (18)) was evaluated with these derivatives for all of the 17,296 combinations formed from chosing three experiments at a time from a total of forty-eight.

The set of experiments were carried in duplicate. The data from all eighteen experiments was then used to update the parameter estimates. These estimates were calculated with criterion B(equation (15)) and the error estimates that had been made previously.

At the same time it was decided to investigate the effect of temperature on the solubility of the precipitates. Five experiments were designed in the same manner described before and carried out at 5°C compared to the usual temperature of 25°C. The equilibrium model was adjusted to accommodate the change in temperature by substituting the values of the free energy constants associated with the reactions of hydrogen and the different anions. These values were either taken directly from the literature or calculated from entropy data when only the latter information was available. The values are recorded in Table 32 of section 1, Appendix IV. Because no other information was available, the same solubility parameters for the orthophosphate and carbonate precipitates were used to design the experiments at the lower temperature. Later, four additional experiments were carried out at 5°C. The initial and final concentrations of all nine experiments are reported in Table 33 of section 1, Appendix IV. The free energy parameters obtained from these results are reported further on.

At this stage in the experimental program, the model and design procedure were changed because of three new developments. First, a set of computer routines based upon Powell's Algorithm (H-6) became available. These programs were substituted for the Simplex algorithm in the experimental design procedure. The grid search was no longer needed to calculate the starting position for the direct search.

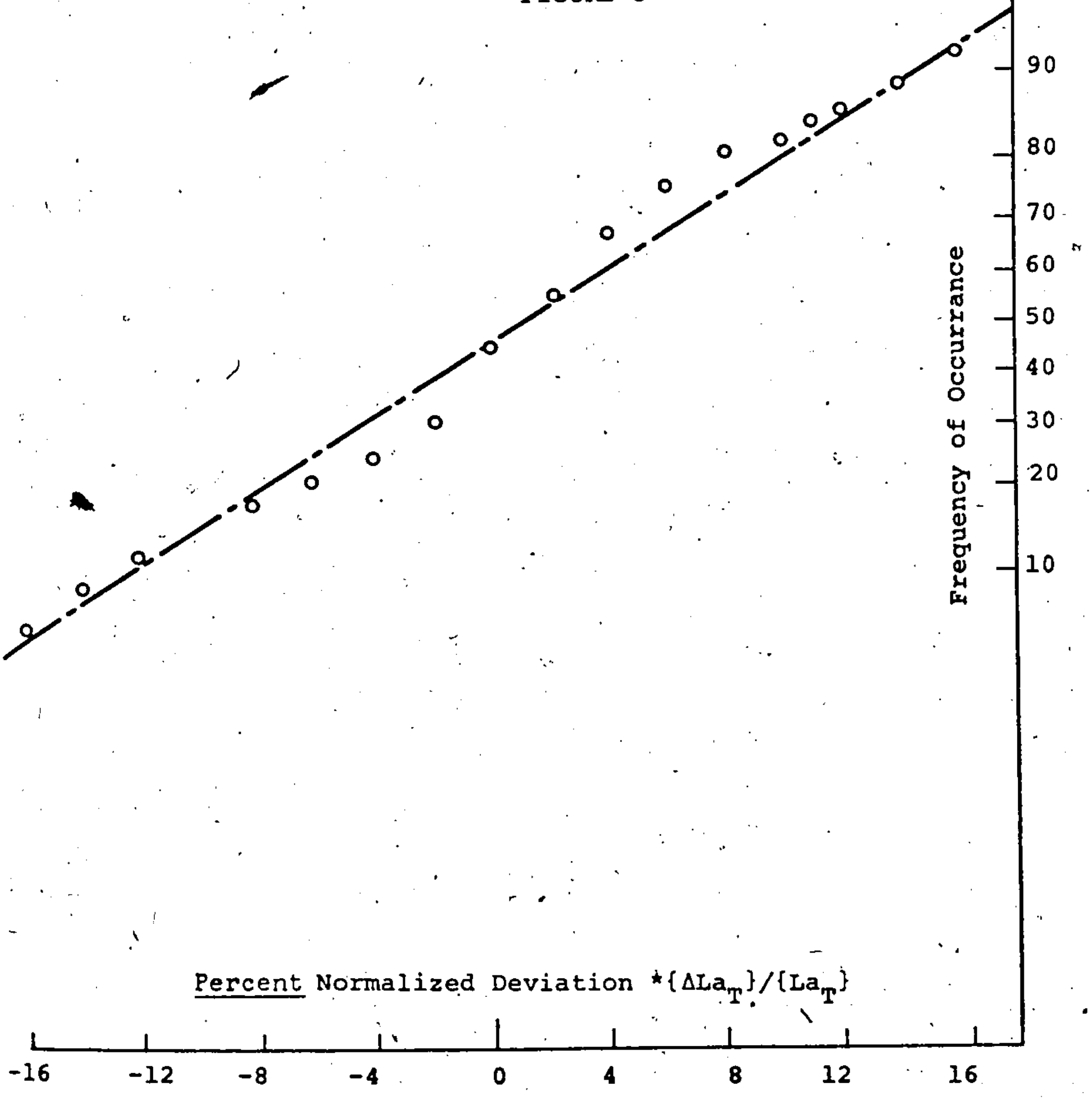
Before any experiments had been performed the equilibrium composition at different initial conditions had to be predicted. The values of the solubility products for the lanthanum phosphate, carbonate and hydroxide precipitates were taken from the literature. These calculations indicated that significant quantities of lanthanum hydroxide would not be formed in the pH range between 7.5 to 9.5, and therefore this reaction was not included. Examination of the results from the first 18 experiments, with mass balances indicated that more lanthanum disappeared from solution than could be accounted for by precipitation with the orthophosphate and carbonate anions. This implied that the hydroxide precipitate had also formed; therefore, this reaction was included again in the model. The orthophosphate and carbonate solubility parameters were re-evaluated from results of the first eighteen experiments. The new parameter estimates and the value assumed for the hydroxide solubility parameter are reported in Table 3.

A sufficient number of experiments had been carried out in duplicate on the three phosphate compounds (as the systems were being investigated simultaneously) to allow an analysis of the errors in the measured quantities. For each type of analysis, the ratios calculated from the deviations measured in a set of duplicate results over the mean of that set were plotted on frequency diagrams. From Figures 3 to 5, it can be seen that in each case the ratios are approximately normally distributed. Thus, it was assumed that the errors in the analyses of the lanthanum, carbonate and phosphate concentrations in solution were constant percentages of the concentrations themselves. For each element, the percentage was estimated as the average value of the appropriate set of ratios. These estimates are reported in Table 5. Because the analyses for the condensed and orthophosphates species were similar, the magnitudes of their errors were assumed to be the same.

It now became possible to calculate a covariance matrix for the observations at each experimental condition. As reviewed in section 1 of Chapter III, this covariance matrix included the effects of errors in the measured quantities (as discussed above) and the independent variables. The properties and estimates assumed for the errors of the independent variables are reported in section 1 of Appendix III. Criterion D_3 (equation (19)) was now used to design the

DISTRIBUTION OF NORMALIZED
DEVIATION IN LANTHANUM
ANALYSIS

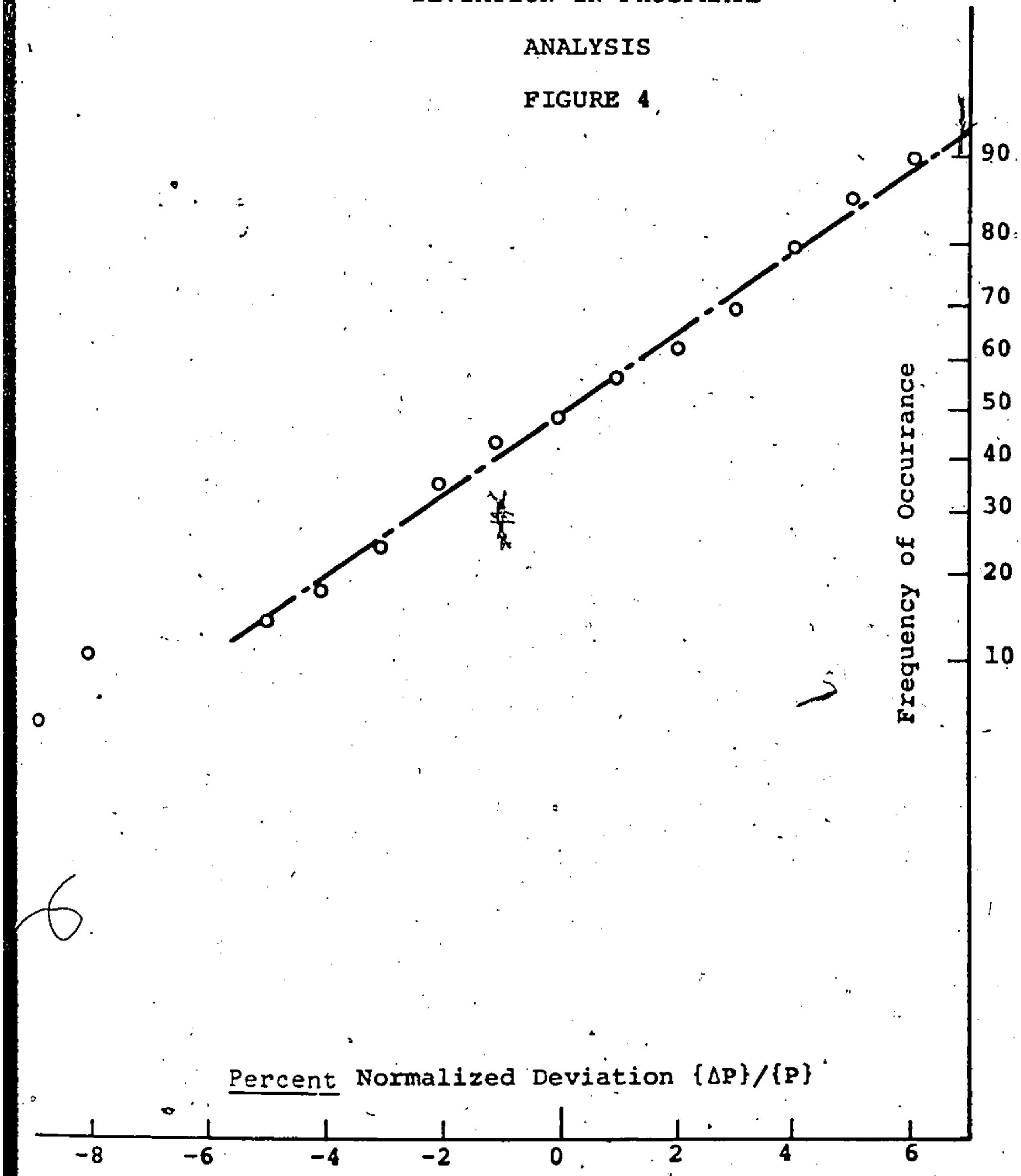
FIGURE 3



*{La_T} is the aqueous lanthanum

DISTRIBUTION OF NORMALIZED
DEVIATION IN PHOSPHATE
ANALYSIS

FIGURE 4



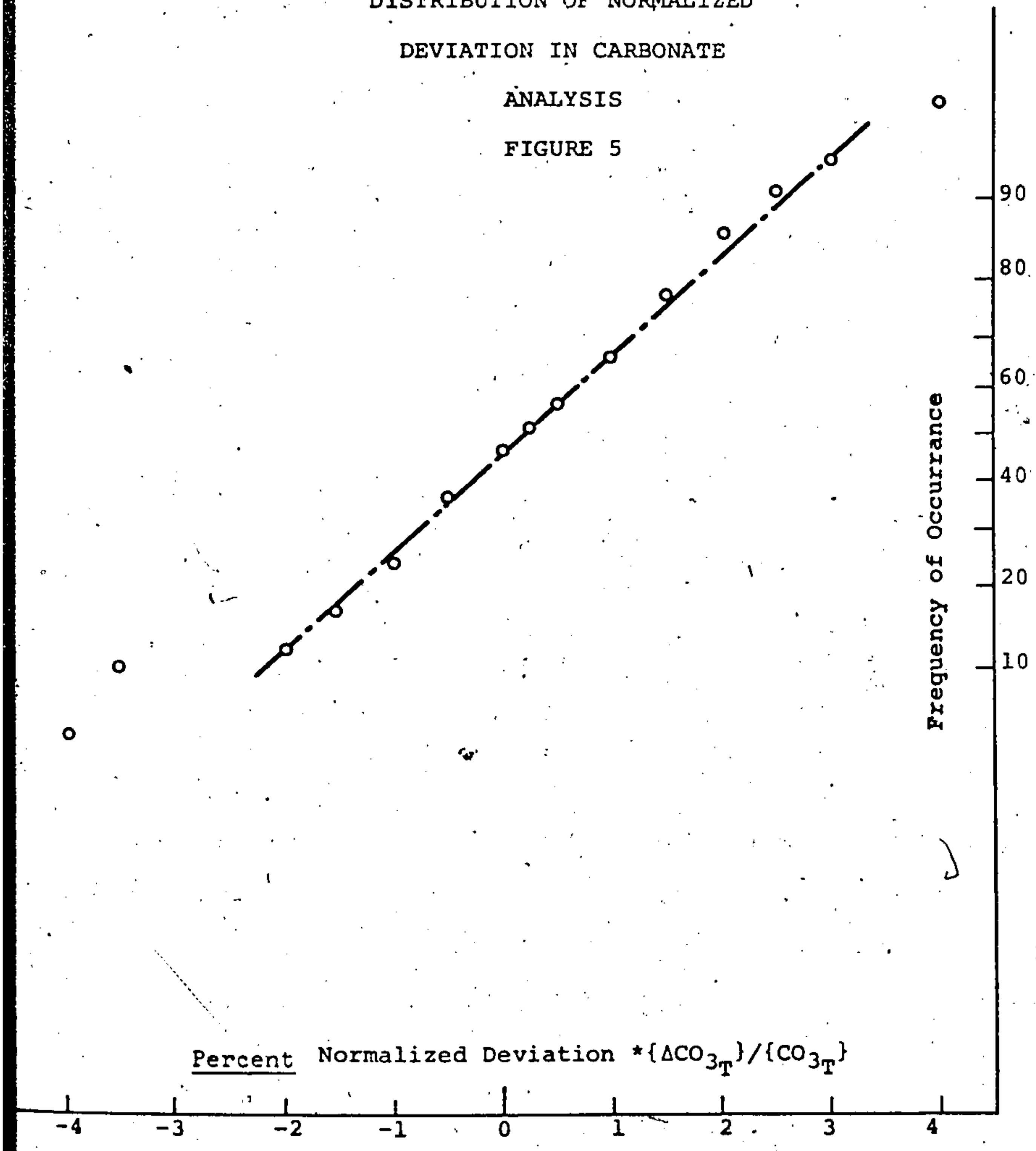
* {P} is the total phosphorus concentration in solution.

DISTRIBUTION OF NORMALIZED

DEVIATION IN CARBONATE

ANALYSIS

FIGURE 5



*{CO_{3_T}} is the total aqueous inorganic carbon concentration

remaining experiments in this section, and criterion B (equation (15)) to estimate free energy parameters.

Two additional sets of three experiments were designed and carried out at 25°C. The initial and final concentrations are reported in section 1 of Appendix IV. To economize on computer time, the first twelve experiments were no longer used to estimate parameters. The decision to stop the experiments was based upon the rate at which the size of the confidence region of the parameters decreased. The relative volume of this region was calculated as the determinant of criterion D_3. Values were determined after the first eighteen experiments, the next set of nine (which comprise the last six experiments and the new set of three), and after twelve experiments as reported in Table 6.

The final estimates of the solubility parameters for the orthophosphate, carbonate, and hydroxide precipitates are recorded in Table 3 along with estimates of their standard deviations. These estimates and the normalized parameter covariance matrix were derived from the experimental design criterion D_3(equation (19)), into which the conditions of the last twelve experiments had been substituted (see section 2, chapter III). The correlation amongst the free energy parameters is indicated by the off-diagonal terms of the normalized matrix. Because these values are close to unity, the three solubility parameters evaluated here are highly correlated. In some cases, the correlation amongst parameters can be avoided by transforming the parameters in the model itself. Unfortunately, the complexity of the nonlinear model used here does not lend itself to this type of operation. It was also hoped that maximizing the experimental design criterion and hence minimizing the parameter covariance matrix would reduce the magnitude of the covariance terms (i.e., off-diagonal elements) relative to the variance terms. In the situation here, this had not happened.

The multiple correlation coefficients (see section 1 of chapter III) indicate the variance which is removed from the observations by the model. Because these coefficients approach unity for both responses, the equilibrium model successfully simulates the correlation between the dependent and independent variables.

Similarly in Table 4, the free energy parameters estimated from the nine experiments carried out at 5°C are presented. These estimates were calculated with criterion B (equation (15)) and the covariance matrix estimated for each set of observations. The solubility parameter for the hydroxide reaction was not evaluated because there is no indication that this precipitate was formed in any of the experiments. An indication of the insoluble salts which are formed, is found by noting the mole ratios at which lanthanum to phosphorus, and lanthanum to carbonates are removed from solution. The normalized parameter covariance matrix indicates that correlation exists between the parameter estimates. The multiple correlation coefficients again show the model is a good representation of the observations. In comparing, the

TABLE 3

MODEL PARAMETERS FOR
La - PO_4 - CO_3 SYSTEM AT 25°C

	Solubility Products of		
	$pKLaPO_4$	$pKLa_2(CO_3)_3$	$pKLa(OH)_3$
taken from the literature	22.43	33.4	not calculated
after twelve experiments	16.81	27.41	not calculated
after initial eighteen experiments	15.93	25.07	20.88*
after nine designed experiments	15.11	24.77	21.31
after twelve designed experiments	15.09	24.93	21.40
standard deviation	± .02	± .05	± .03

NORMALIZED
PARAMETER COVARIANCE
MATRIX

1.	.94	.91
.94	1.	.888
.91	.888	1.

MULTIPLE CORRELATION COEFFICIENT

Orthophosphate Response	0.99
Carbonate Response	0.99

*(assumed from literature)

TABLE 4

MODEL PARAMETERS FOR La – PO_4 – CO_3 SYSTEM AT 5°C

	pK_{LaPO_4}	$pK_{La_2(CO_3)_3}$
after nine experiments	16.6	29 .7
standard deviation	± .20	± .46

NORMALIZED PARAMETER COVARIANCE MATRIX

1.	0.99
0.99	1.

MULTIPLE CORRELATION COEFFICIENT

Orthophosphate Response	0.99
Carbonate Response	0.99

TABLE 5

ESTIMATED VARIANCE OF THE DEPENDENT VARIABLES

Variable	Units	Variance
Lanthanum	(MgLa/1)	$(.1071 * [La]_T)^2$
Carbonate	($MgCO_3$/1)	$(.0137 * [CO_3]_T)^2$
Phosphate	(MgP/1)	$(.0318 * P_T)^2$

$[La]_T$, $[CO_3]$, and P_T refer to the total concentration of that element in solution

TABLE 6

RELATIVE VOLUME OF THE CONFIDENCE REGION OF THE MODEL PARAMETERS

No. of Experiments Performed	Relative Volume
initial eighteen	2.047×10^{-3}
nine designed experiments	1.278×10^{-4}
twelve designed experiments	$.660 \times 10^{-4}$

the solubility of the carbonate precipitate is more strongly influenced by the solution temperature.

IV.3 Lanthanum - Tripolyphosphate Solubility

Baxter (B- 6) found that two soluble complexes are formed from the combination of the lanthanum and tripolyphosphate ions. These complexes are $LaP_3O_{10}^{-2}$ and $LaHP_3O_{10}^{-1}$. The stability constants for these complexes were found to be:

(i) $B_1 = (LaP_3O_{10}^{-2})/(La^{3+})(P_3O_{10}^{-5}) = 3.63 \times 10^6$

(ii) $B_2 = (LaHP_3O_{10}^{-1})/(La^{3+})(H^+)(P_3O_{10}^{-5}) = 5.12 \times 10^{11}$

at the temperature of 20°C and an ionic strength of 0.1 $(CH_3)_4NCl$.

Baxter also investigated the precipitation of the tripolyphosphate with lanthanum by the hydrogen ion displacement method. He concluded that the normal lanthanum salt precipitated with reactant concentrations at the millimole level, though no quantitative solubility data was presented.

Based upon Baxter's studies, the equilibrium model of the tripolyphosphate system included the formation of two soluble complexes and the precipitation of the normal salts. The objective was to determine estimates of the free energy parameters for these three reactions. The species, components, set of reactions and those free energy parameters which were assumed to remain constant are reported in Table 34 of section 2, Appendix IV. The independent variables in these experiments were the initial lanthanum, tripolyphosphate and hydrogen ion concentrations. The measured responses were the aqueous lanthanum and phosphorus concentrations after precipitation in those experiments carried out at 25°C, and only the latter element for the experiments at 5°C. The final solution pH was also measured. Initial estimates of the free energy parameters of the tripolyphosphate complexes (see Table 7) were Baxter's values which were corrected to zero ionic strength. This correction was made with the Davies equation, (see section 7, Appendix II). An approximate measurement of lanthanum tripolyphosphate solubility was determined from a preliminary experiment.

Because information concerning the errors in the observations was as yet incomplete, the first six experiments were designed with criterion D_1(equation (16)). The levels of the independent variables were selected by means of a grid search. An eighteen point grid was constructed from the partial derivatives of the model responses taken with respect to the following initial concentrations of the independent variables:

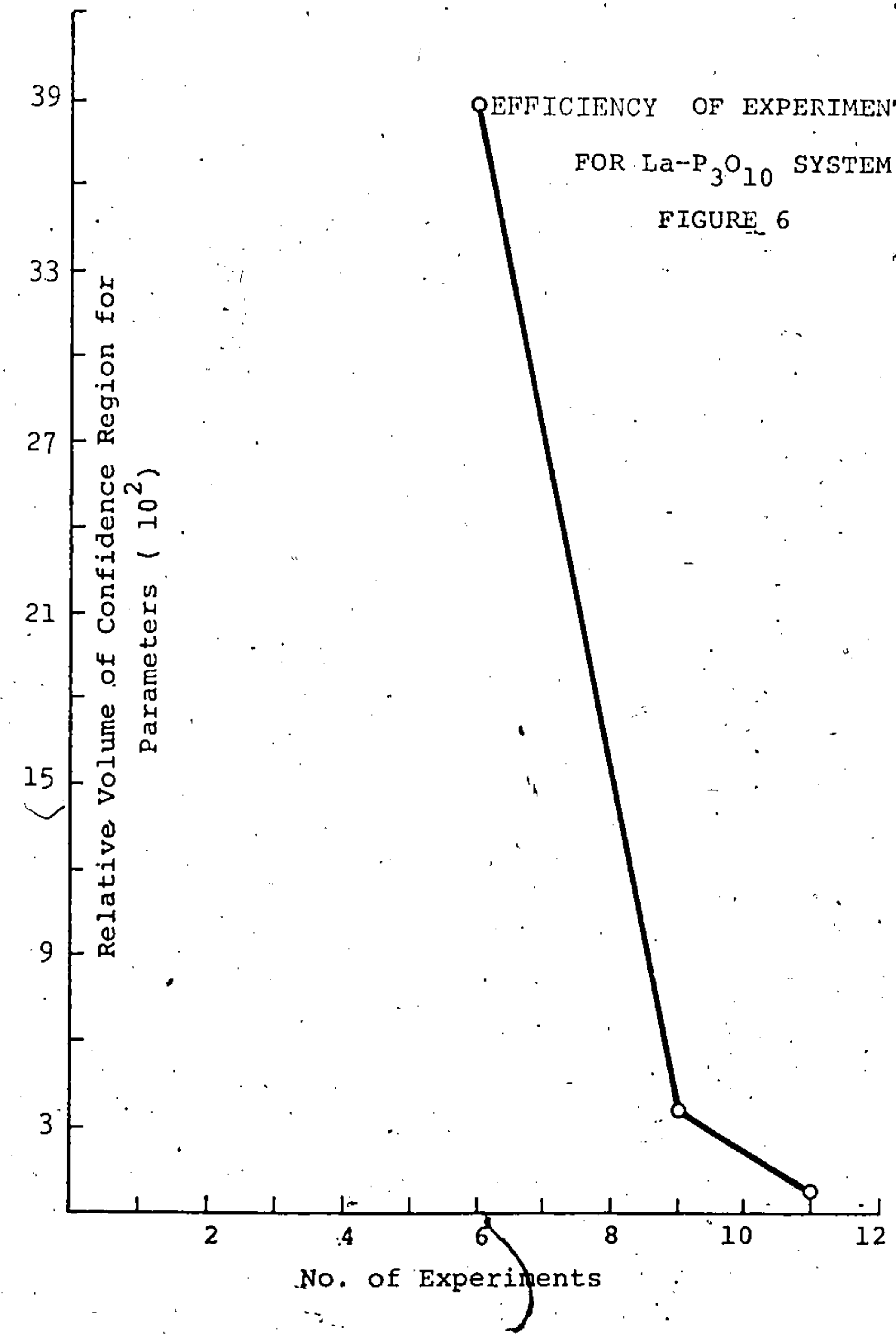
(i) lanthanum - 0.25, .5, and 0.75 mM/l,
(ii) tripolyphosphate - 0.125, 0.25 and 0.375 mM/l,
(iii) hydrogen ion concentration needed to maintain a final solution pH of 5 and 8.

The four experiments in which the total number of moles of tripolyphosphate exceeds that of lanthanum were considered infeasible. Preliminary experiments had indicated that at this condition the strong chelating properties of the anion would prevent precipitation. To select a set of six experiments from a possible fourteen, 3,003 combinations were examined.

From an examination of the entropy and enthalpy data reported in the literature (see section 10, Appendix I) for hydrogen tripolyphosphate complexes, it was determined that their free energy parameters changed by less than 5 percent when the standard temperature dropped from 25 to 5°C. Thus, the six experiments were repeated at the lower temperature. The initial and final concentrations measured in both sets of experiments are reported in Table 35 of section 2, Appendix IV.

From a mass balance calculated for each experiment at 25°C, it was possible to determine the molar ratio in which the phosphate anion and lanthanum cation precipitated from solution. The average value of this ratio for the first six experiments was calculated to be 0.557 as reported in Table 9. Similarly, in later experiments the average value of this ratio remained below the theoretical value of 0.6. After each set of experiments, the hypothesis was tested that the true value of this ratio was 0.6 by a t-statistic. The estimate of variance associated the average value was determined from the data itself. In every case, the hypothesis proved false. The stoichiometry as measured from the experiments was therefore substituted for this reaction in the computer model.

Free energy parameters were calculated using criterion A (equation (13)) from the data of the first six experiments at 25°C. Five additional experiments were designed and carried out in groups of three and two. Sufficient information about



EFFICIENCY OF EXPERIMENTS FOR La-P_3O_{10} SYSTEM

FIGURE 6

the observation errors was available to estimate a covariance matrix for each experimental condition and use the design criterion D_3(equation (19)). Also, criterion B (equation (15)) was now used to determine free energy parameters. The relative size of the confidence region in parameter space was calculated from the design criterion after each set of experiments and plotted as shown in Figure 6. From this graph, it becomes evident that the errors in the free energy parameters are not reduced significantly more after eleven experiments.

The final parameter estimates are shown in Table 7 and 8 for the experiments carried out at 25°C and 5°C. Because the multiple correlation coefficients in every case are close to unity (see section 1, Chapter III), the equilibrium models accurately simulate the observations. The normalized covariance matrix which was evaluated from the elements of the design criterion D_3 (see section 3, Chapter III) indicate that the estimates of the free energy parameters for the soluble complexes are not highly correlated, while the estimates for the second complex and solubility parameter are. Estimates of the standard deviation in the parameter estimates are quoted in every case except for the first lanthanum ion complex calculated at the lower temperature. The error estimate for this parameter was so high as to be meaningless. Because error estimates are obtained from the design criterion, they are related to the partial derivatives of the model response taken with respect to the free energy parameter (see equation

TABLE 7

MODEL PARAMETERS FOR La - P_3O_{10} SYSTEM AT 25°C

	Complexes		Solubility Product
	$pKLaP_3O_{10}^{2-}$	$pKLaHP_3O_{10}^{-}$	$pKLa_5(P_3O_{10})_3$
initial values	-9.7*	-14.7*	57.7
after six experiments	-11.4	-16.4	57.9
after nine experiments	-11.4	-17.7	60.3
after eleven experiments	-11.4	-17.7	60.4
standard deviation	± .1	± .14	± .38

NORMALIZED PARAMETER COVARIANCE MATRIX

$$\begin{array}{ccc} 1. & .17 & .193 \\ .17 & 1. & .99 \\ .193 & .99 & 1. \end{array}$$

MULTIPLE CORRELATION COEFFICIENT

Lanthanum-Response	0.99
Tripolyphosphate Response	0.99

*Baxter's estimates corrected for zero ionic strength.

TABLE 8

MODEL PARAMETERS FOR LaP_3O_{10} SYSTEM AT 5°C

	Complexes		Solubility Product
	$pKLaP_3O_{10}{}^{2-}$	$pKLaHP_3O_{10}{}^{-}$	$pKLa_5(P_3O_{10})_3$
after six experiments	-7.76	-18.0	59.7
standard deviation		± 1.15	± 3.16

PARAMETER

<u>Correlation Matrix</u>

0.29	1.	0.99
0.23	0.99	1.

MULTIPLE CORRELATION COEFFICIENT

Tripolyphosphate Response 0.99

TABLE 9

La - P_3O_{10} SYSTEM AT 25°C

No. of Experiments	Ratio Average	Ratio Variance	t-Value Measured	tabulated at 95% *
	Molar Ratio of Tripolyphosphate to Lanthanum in the Solid Phase			
6	.557	.007	6.15	2.015
9	.552	.006	8.	1.860
11	.551	.006	8.16	1.812

(17)). In this case, the error estimate is related to the inverse of the root mean square of the sum of these derivatives evaluated at each experimental condition. When the derivative is small, the error estimate becomes large. A very low value for the derivative indicates that the equilibrium concentration of phosphate is hardly dependent upon this parameter and thus the formation of corresponding species. The experiments at the lower temperature were carried out in a pH range where the formation of the lanthanum tripolyphosphate complex was not favoured.

In comparing the parameters in Tables 7 and 8, it can be concluded that neither the formation of the lanthanum hydrogen tripolyphosphate complex nor the precipitation of the normal salt is strongly dependent upon temperature in the interval of interest.

IV.4 Lanthanum - Pyrophosphate Solubility

Baxter (B-6) also studied the reactions between lanthanum and the pyrophosphate anion by means of pH and conductance titrations. Again he found two complexes $LaP_2O_7^{-1}$ and $LaHP_2O_7$ whose stability constants he estimated as:

$$\text{(i)} \quad B_1 = \frac{LaP_2O_7^{-}}{(La^{3+})(P_2O_7^{-4})} = 4.56 \times 10^6$$

$$\text{(ii)} \quad B_2 = \frac{(LaHP_2O_7)}{(La^{3+})(P_2O_7^{-4})(H+)} = 6.06 \times 10^9$$

in an aqueous solution whose temperature is 20°C and ionic strength 0.1 $(CH_3)_4NCl$. Baxter also carried out a qualitative study of the precipitation of lanthanum pyrophosphate. He observed that the normal salt $La_4(P_2O_7)_3$ precipitated initially from solution in all cases, but if the solution contained a molar excess of sodium pyrophosphate compared to lanthanum a double salt, $La_4(P_2O_7)_3Na_4P_2O_7.10H_2O$ began to crystalize after 2 to 3 days. Baxter reported no quantitative information concerning the solubility of the lanthanum pyrophosphate salts.

Sheka and Simyavskaya (S-6) have studied both the solubility and complex formation of lanthanum pyrophosphate. Their methodology was based on the analysis of solubility curves of lanthanum pyrophosphate. They, as Baxter, also found the existence of two salts, normal and double sodium salts. Their observations led to the conclusion that only the normal salts were precipitated in the pH range of 5.7 - 10.2, if the molar ratio of pyrophosphate to lanthanum is less than 1. The following stability constants were calculated for the ion complexes. These values are reported for 25°C and at ionic strength corrected to zero.

$$B_1 = (LaP_2O_7^{-1})/(La^{3+})(P_2O_7^{-4}) = 5.25 \times 10^{16}$$

$$B_2 = (La_2P_2O_7^{2+})/(La^{3+})^2(P_2O_7^{-4}) = 4.26 \times 10^{19}$$

$$B_3 = (La)(P_2O_7)_2^{-5}/(La^{3+})(P_2O_7^{-4})^2 = 3.72 \times 10^{18}$$

Because in the experiments here and later in wastewater the molar ratio of pyrophosphate to lanthanum is expected to be less than one, only the precipitation of the normal salt was considered in the equilibrium model. Also to be consistent with the tripolyphosphate reactions, the ionic complexes suggested by Baxter were used.

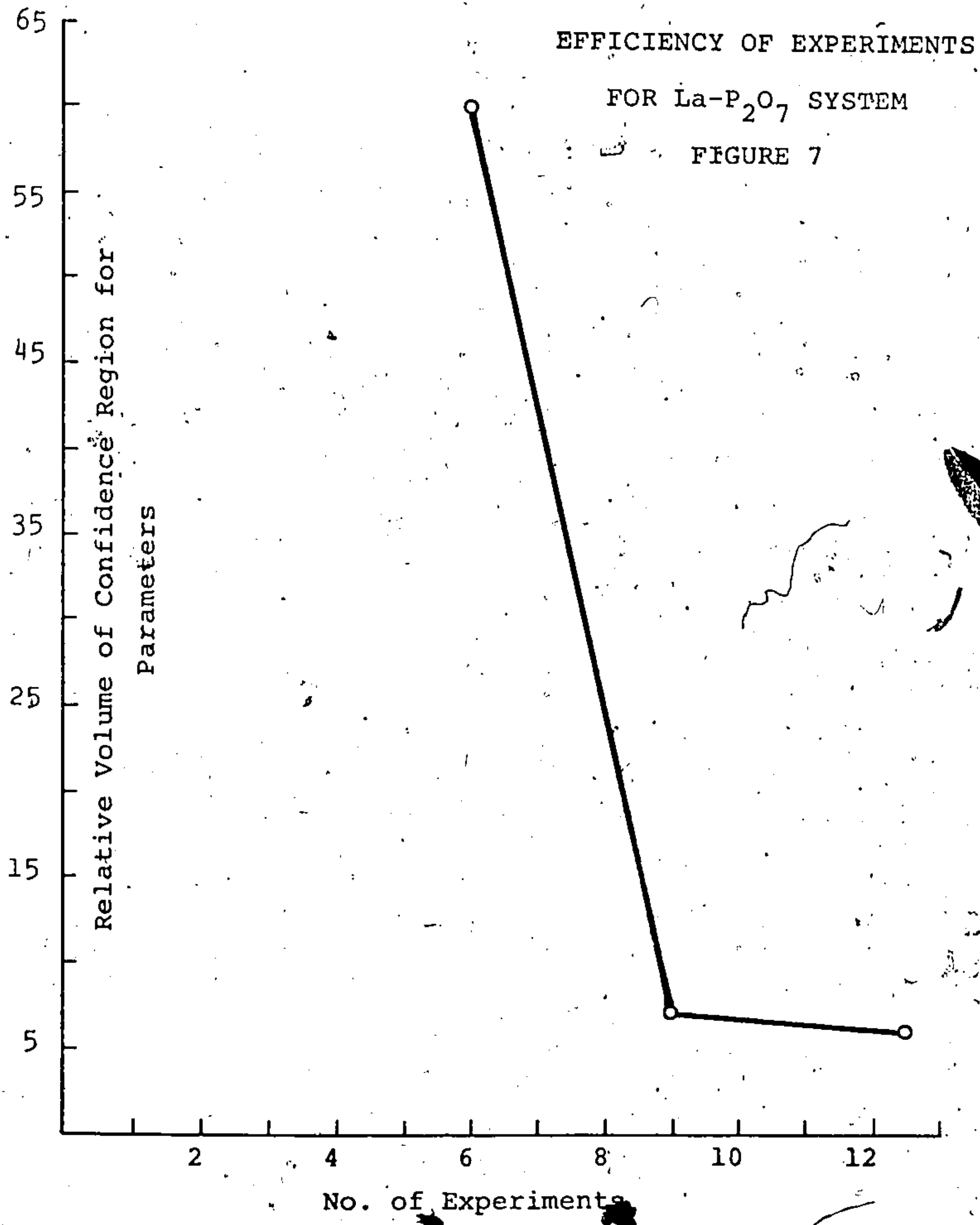
The objective here was to estimate the free energy parameters for two ionic complexes and the lanthanum pyrophosphate precipitate. The species, components, reactions, and those free energy parameters assumed to remain constant in the equilibrium model are reported in Table 36 of section 3, Appendix IV. The independent variables for the model are the initial concentrations of lanthanum, pyrophosphate and hydrogen ion. The influence of these variables on the chemical system is determined by measuring the final concentrations of the lanthanum and pyrophosphate in solution. The solution pH at equilibrium was also measured. Initial estimates of the free energy parameters for the lanthanum pyrophosphate complexes were derived from Baxter's values corrected to zero ionic strength as in the previous study. The solubility of the pyrophosphate precipitate was assumed to be similar to that of tripolyphosphate.

As in the previous study, a grid search was used to select the first experiments. In this case however, no particular set of experiments were found to be better than any other. Thus, three experiments were arbitrarily chosen and carried out at 25°C and 5°C. The initial and final concentrations of the variables are reported in Table 37 of section 3, Appendix IV. The first set of free energy parameters reported in Table 10 were calculated using criterion A (equation (13)).

Ten further experiments in sets of three and four were designed and carried out. At this point in the program it was possible to calculate the full covariance matrix of the observations for each experiment. Therefore criterion D_3 (equation (19)) was used to design these experiments and criterion B(equation (15)) to estimate parameters from them. A record of the change in size of the confidence region in parameter space was kept after the sixth experiment. From Figure 7, it is evident that the increase in the certainty of the parameter estimates after thirteen experiments is slight. Thus this part of the program was concluded.

In the same manner as for the tripolyphosphate precipitate, the average molar ratio in which pyrophosphate and lanthanum precipitated from solution was determined. Estimates of the average value of this ratio and its variance are reported in Table 12. Unlike the previous situation, the hypothesis that the average ratio is an estimate of the theoretical value of 0.75 was not disproved. Thus, this reaction was represented by the ideal stoichiometry in the computer model.

The final estimates of the free energy parameters for the lanthanum pyrophosphate reactions are reported in Tables 10 and 11. The estimated standard deviation of that parameter



EFFICIENCY OF EXPERIMENTS FOR La-P_2O_7 SYSTEM

FIGURE 7

which belongs to the lanthanum hydrogen pyrophosphate complex was found to be extremely large and thus not reported. As discussed before, these error estimates are calculated from the inverse matrix of the design criterion D_3 (see section 3, Chapter II). The estimates are therefore related inversely to the partial derivatives of the model response taken with respect to the parameters. The derivatives taken with respect to this parameter were always two and in some cases six orders of magnitude less than the others. Because of this situation, the error estimate of this parameter will be extremely large. Also it was observed that the concentration of the $LaHP_2O_7$ complex was always two orders of magnitude less than the concentration of $LaP_2O_7^-$. Therefore, the presence of the former species and reaction has no significant influence in simulating the data. To simplify the model, this species was removed. Only the elements of the parameter covariance matrix belonging to the complex $LaP_2O_7^{-1}$ and the precipitate are reported. A moderate degree of correlation is seen to exist. The same two parameters were evaluated from the experiments at 5°C and are reported in Table 11. Even less correlation is seen to exist for this set of parameters. The influence of temperature on these parameters appears to be moderate and causes a greater change in their values than could be attributed to uncertainty in the estimates themselves. The multiple correlation coefficients indicate in every case (see section 1, Chapter III) that the equilibrium model simulates the

TABLE 10

MODEL PARAMETERS FOR La – P_2O_7 SYSTEM AT 25°C

	Complexes		Solubility Product
	$pKLaP_2O_7^-$	$pKLaHP_2O_7$	$pKLa_4(P_2O_7)_3$
after three experiments	-8.14	-11.77	49.0
after six experiments	-6.58	-10.30	59.3
after nine experiments	-11.50	-12.14	57.4
after thirteen experiments	-10.64	-12.52	54.6
standard deviation	± .06		± .17

NORMALIZED
PARAMETER COVARIANCE
MATRIX

1.	.86
.86	1.

MULTIPLE CORRELATION COEFFICIENT

Lanthanum Response	0.99
Pyrophosphate Response	0.99

TABLE 11

MODEL PARAMETERS FOR La - P_2O_7 SYSTEM AT 5°C

	Complex	Solubility Product
after three experiments	-10.43	53.6
standard deviation	±.08	+ .14

NORMALIZED PARAMETER COVARIANCE MATRIX

1.	.51
.51	1.

MULTIPLE CORRELATION COEFFICIENT

Lanthanum Response	0.99
Pyrophosphate Response	0.99

TABLE 12

La - P_2O_7 SYSTEM

	Molar Ratio of Pyrophosphate to Lanthanum in the Solid Phase			
No. of Experiments	Ratio Average	Ratio Variance	t-Value Measured	Tabulated at 95%
3	.716	.034	1.	2.920
6	.729	.018	1.11	2.015
10*	.738	.024	.5	1.833

*For three of the experiments the ratio could not be evaluated.

experimental observations quite well.

IV.5 Investigation into the Expected Distribution of Phosphates in Wastewater

Before considering experiments in which the simultaneous removal of all three phosphate species was to be investigated, two questions had to be answered. First, an estimate was needed of the range of concentrations of ortho-, pyro-, and tripolyphosphate present in untreated wastewater. Second, the question arose as to what extent this initial distribution of phosphates would change as the wastewater is subjected to secondary treatment.

It is widely known that the rate of hydrolysis of condensed phosphates is accelerated during the secondary biological treatment step. This results in orthophosphate being the dominant species in the secondary effluent. The same conclusions were reached by Heinke (H-2) in his studies. Heinke also concluded that in general the rates of hydrolysis of tripoly- and pyrophosphate were independent of each other and that the latter rate was slower. This second observation could lead to the possibility that pyrophosphates may become the dominant species at some point in the sewage treatment process.

Samples were taken at random from three sewage treatment plants in the local area. These samples were from the primary influent stream and were analyzed for their phosphate distribution by the differential technique. As only the soluble species were of interest, the samples were filtered through a 0.45 micron membrane filter. The phosphate distribution of these samples is reported in Table 13. The distribution in a sample taken by Heinke five years earlier at the Dundas Sewage Treatment Plant, is also included.

Examination of these results indicate a wide variation in the distribution of soluble phosphate species. Certain trends are, however, indicated. In all of the recent samples orthophosphate is seen to be the dominant species followed closely by tripolyphosphate. Pyrophosphates appears as a minor species never reaching more than 10 percent of the total soluble phosphorus concentration. In comparison to Heinke's analysis, presence of tripolyphosphate has decreased in primary effluents. This may be a direct result of the recent requirement for the reduction of phosphorus content in household detergents as specified by the Ministry of Enviroment, (see section 2, Appendix I). In household detergents, phosphates are present in a condensed form, 80 percent of which is usually tripolyphosphates. These observations also differ from the statement made by Leckie and Stumm (L-3), who considered pyrophosphate as the most important polyphosphate constituent in a domestic wastewater.

Before the advent of the liquid chromatographic technique for phosphate analysis, studies of condensed phosphate hydrolysis occurring in wastewater had been reported on the basis of the reduction of the total condensed phosphorus

TABLE 13

OBSERVED SOLUBLE PHOSPHATE DISTRIBUTION IN PRIMARY EFFLUENT

S.T.P.*	Year Sampled	Percentage of Species			Total Phosphate (Mg-P/1)
		Ortho-	Pyro-	Poly-	
Dundas	1968**	29.0	7.9	63.1	6.85
Dundas	1973	93.8	1.3	4.9	4.9
Burlington (Skyway)	1973	50.9	7.4	41.8	5.50
		62.4	9.2	28.4	3.26
		93.5	0.4	6.1	2.48
Hamilton	1973	100.			.33

*Sewage treatment plant location.

**Data as reported by Heinke.

concentration. This reaction was reported as first order. Heinke, in his studies of wastewater systems, followed the same convention. It was desired, however, to have estimates of the rate constants for hydrolysis reactions of each species in wastewater.

A kinetic model was proposed based upon the assumption that the hydrolysis reactions could be represented by following a set of irreversible series-parallel reactions.

$$TPP + H_2O \longrightarrow PP + OP \qquad (21)$$

$$PP + H_2O \longrightarrow 2OP \qquad (22)$$

where (i) TPP are the tripolyphosphate species,
(ii) PP are the pyrophosphate species,
(iii) OP are the orthophosphate species.

The integrated rate expressions of this kinetic model were programmed. The reaction rates were assumed to be either zero or first order with respect to the concentrations of the condensed phosphates. The listings of the three subroutines (each containing the rate expression for one species) are reported in Appendix VI.

The experimental data was taken from the work reported by Heinke (page 277, Figure 40-3). Heinke had monitored the changes in the ortho-, tripoly-, and pyrophosphate concentrations with the differential analysis in a sample of primary effluent from the Dundas Sewage Treatment Plant. This experiment had been carried out at 20°C, under alternate day and night lighting, and at a constant solution pH of 9. This particular set of data had been selected because the total concentration of phosphorus in solution had remained constant.

Because Heinke had observed the average rate of hydrolysis in wastewater to be first order, rate constants were estimated for the expressions of the same order. These estimates were determined with the ortho- and tripolyphosphate concentrations with criterion A (equation (13)). The values are:

(i) tripolyphosphate hydrolysis---8.612 x 10^{-3} (l/hrs.)

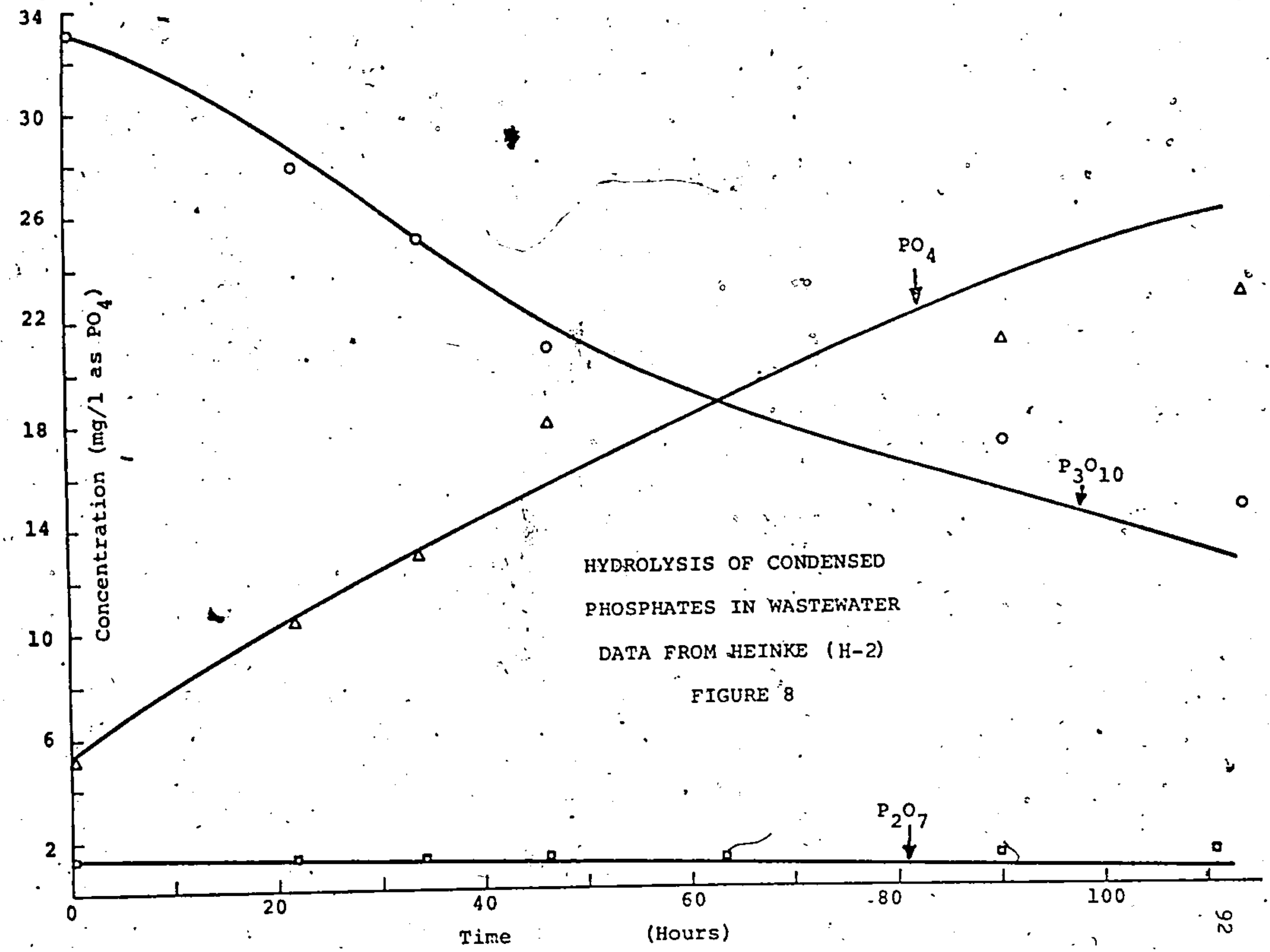
(ii) pyrophosphate hydrolysis------1.066 x 10^{-1} (l/hrs.)

Heinke had estimated the average rate for both condensed Phosphates to be 7.2 x 10^{-3} (l/hrs.). A comparison of the kinetic model's predictions to the experimental data is shown in Figure 8.

If one compares the ratio of the hydrolysis rate constants to the ratio of the initial polyphosphate concentrations reported in Table 13, one finds that pyrophosphates hydrolyze at a faster rate. It can be expected that the concentration of this species will not increase during wastewater treatment. The distribution of phosphate species is expected to change from its initial value in the influent to the situation in which orthophosphate is the dominant species. Pyrophosphate will always remain as a minor constituent.

IV.6 Lanthanum-Phosphorus Precipitation in Distilled Water

Nine experiments were performed in which lanthanum was used to precipitate a mixture of the three phosphorus



HYDROLYSIS OF CONDENSED PHOSPHATES IN WASTEWATER

DATA FROM HEINKE (H-2)

FIGURE 8

compounds, tripoly-, pyro-, and orthophosphate in distilled water. These experiments evaluated the efficiency of the removal process in a mixed environment, and provided a base case with which to compare the equilibrium model predictions. Solubility and ion complexing parameters of this model were estimated from the previous series of experiments, in which only one phosphate compound was present at any one time.

All the solutions were prepared and diluted with double distilled water. In the three distributions of soluble phosphates, the ratio of tripoly- to pyro- to orthophosphate (in mg P/l) was set approximately at either 1:3:1, 2:2:1, or 3:1:1. The initial total concentration of phosphorus was between 19 and 20 mg P/l. The selection of these distributions was based upon the observations made in the previous study of wastewater influents. The initial lanthanum chloride concentration was selected to satisfy the precipitation of all phosphates as their normal salts on a stoichiometric basis. The inorganic carbon and sodium chloride concentrations were set for all experiments at 240 mg/l CO_3^{-2} and 143.5 mg/l NaCl, (i.e., levels normally found in wastewaters).

The reactants were added as aliquots from stock solutions in order of decreasing alkalinity to keep the solution basic. Lanthanum chloride was added after the phosphates to prevent the precipitation of the metal only as a hydroxide. The solution was diluted to 200 ml, mixed and the pH adjusted to 6.5, 8., or 9.5 by addition of 1 M HCl. This pH range is typical of the values found in sewage. During the pH adjustment, air was bubbled through the solution to insure that it was at equilibrium with the atmosphere. The air was filtered, humidified, and then introduced through a sintered glass diffuser.

A sample was then diluted to 250 mls, stoppered, placed in a shaker in a temperature enviroment controlled at 25^oC. A period of one hour was found sufficient for the sample to reach ambient temperature. After this time, sample pH was measured. If no significant change in solution pH from the previously measured value was found, this was taken to be indicative that the precipitation reaction had reached equilibrium. If a change was noted, the sample was placed back on the shaker and the solution pH measured again later. After the solution pH had stabilized, the solid phase was removed first by centrifuging and then filtration through a 0.2 micron membrane filter. In the acidic solutions, distinct floc particles were formed which would settle. In the basic solutions, a cloudy dispersion which did not settle was observed. The filtrates appeared clear and no change in the soluble phosphate concentration was noted when a sample was passed a second time through a fresh filter. The filtrate was analyzed for the following elements:

(i) soluble phosphate species by a differential analysis,
(ii) lanthanum ion by flame emission,
(iii) inorganic carbon with the carbonaceous analyzer.

The initial and final concentrations are reported in Table 38 of section 4 of Appendix IV. A comparison of the predictions of the computer model to the observations is presented in the next chapter.

IV.7 Lanthanum-Phosphorus Precipitation in Wastewater

The efficiency of lanthanum in precipitating a mixture of the three phosphate compounds from wastewater was evaluated. This data was then compared to the predictions of the computer model which described these precipitation reactions.

A sample of primary influent was obtained from the Burlington Skyway Treatment Plant. This sewage treatment plant, located in Burlington, Ontario operates an extended aeration mode on influent that can be characterized as typically domestic. The average flowrate to the plant is 8 million gallons per day. The influent sample was taken from the primary grit chamber.

On site, the sample was passed through a funnel packed with fine fibreglass wool. At the laboratory, it was then necessary to pretreat the wastewater sample to inhibit biological activity, while it was being stored. Since the wastewater contained soluble organic carbon and is innoculated with microorganisms, it is an ideal growth medium. While achieving inhibition, it is also desired to minimize alteration of the chemical characteristics of the sample. To remove the innoculant, a presterilized-disposable filter apparatus with a 0.2 micron membrane filter was used. The samples were then stored at 1°C until required for testing. A summary of the chemical analyses that are normally used to characterize water quality is presented in Table 40 of section 5, Appendix IV for these samples.

Nine experiments were carried in a manner similar to before but substituting wastewater as the dilution medium. In all of the experiments, the initial composition was altered by additions from standard stock solutions. The solution pH was adjusted to either 6.5, 7.5 or 8.5 by an automatic titrator and during this time the sample was brought into equilibrium with the atmosphere by means of an air sparge. As before, the solutions were thermostated at 25°C and kept mixed until the pH remained constant. In every sample, distinct floc particles formed which would settle out under quiesent conditions. The particles were separated by filtration with a 0.2 micron filter. The concentrations of the following components in the filtrate were measured:

(i) phosphates by differential analysis,

(ii) lanthanum ion by flame emission,

(iii) calcium and magnesium ions by atomic absorption spectroscopy,

(iv) organic and inorganic carbon with the carbonaceous analyzer.

In the first two sets of experiments, the initial phosphate concentrations were altered. The lanthanum dosage was determined by the stoichiometric requirement to precipitate all of the phosphates as their normal salts. The important change in the second set of experiments was to increase the initial concentration of calcium ion by 75 percent. In the third set, the initial distribution of phosphates was changed and only 87 percent of the stoichiometric requirement of lanthanum was added. The initial and final concentrations measured in all of the solutions is reported in Table 39 of section 5, Appendix IV. The observed removal is compared to the computer model predictions in the next chapter.

V EXPERIMENTAL RESULTS

The predictions by the computer model of the efficiency of phosphorus removal are compared to observations in two different aqueous systems. The first is a distilled water system, in which lanthanum was the sole precipitating agent reacting with a mixture of phosphate species. Second is a wastewater influent, in which magnesium and calcium were also present as possible precipitating cations, sulphate as a complexing anion and an unknown population of organic species. The latter group could only be characterized by their total carbon concentration. The computer model was also turned about to predict the lanthanum dosage required to meet a specific level of phosphorus removal after the water quality of a sample had been specified. This "dosage model" was run under twenty-four separate cases to assess the effects of different water quality parameters on dosage requirements.

V.1 Phosphate Removal-Distilled Water

The computer model of the distilled water system is composed of ten chemical components which enter into twenty-seven reactions in the gas, liquid, and solid phases. These reactions can be classed as:

(i) precipitation reactions, (phosphates, hydroxides & carbonates)

(ii) association and ion complexing reactions in the aqueous phase,

(iii) equilibrium of carbon dioxide (@ $P_{CO_2} \cong 3 \times 10^{-4}$ atm) and aqueous carbonate species.

These reactions along with their free energy parameters are listed in matrix form in section 1, of Appendix V.

The aqueous concentration of an element or compound at equilibrium is specified by point value and an interval. This interval reflects the uncertainty in the model's predictions due to errors:

(i) in estimates of the model parameters;

(ii) in initial concentrations of components,

(iii) in experimental observations.

The magnitude of this interval is calculated as the product of the effective error estimate and the Student's t ratio. This statistic (with a value of 2.86) is evaluated at the 99 percent confidence interval and nineteen degrees of freedom, (i.e., the lowest number associated with a set of parameter estimates). Effective error estimates are obtained from equation (20), (see section 3, Chapter III). The covariance matrices belonging to the parameters, Covar (β) and the independent variables Covar (X_u) are reported in Table 43 and 44 of section 1, Appendix V. Estimates of the errors in the measuring of the lanthanum and carbonate concentrations were obtained from the functions listed in Table 5. The errors associated with determining the concentrations of all three phosphate compounds with the differential technique are a function of the errors in measuring the total phosphorus concentration and the distribution of species. Estimates were obtained from the analysis reviewed in section 7 of Appendix IV.

The model's predictions of the residual phosphate concentration in acidic solutions were observed to always be higher than the concentrations measured. The data used to estimate the lanthanum orthophosphate free energy parameter had been obtained from experiments carried out under basic conditions. This constraint upon pH was used to retain the carbonate species in solution. It was also observed from the computer that the distribution of soluble orthophosphate species changed considerably as the solution pH moved above 7. The dihydrogen phosphate complex which was the dominate species below pH 7, was no longer so in basic solutions. This meant that this reaction had a negligible influence upon the prior estimate of the orthophosphate free energy parameter.

It was decided that the solubility parameter needed to be re-evaluated for the acidic condition. The dependence of solubility parameters upon the solution pH has been observed in previous investigations. For example, Ferguson and McCarty (F-2) found it necessary to define sets of solubility parameters for calcium orthophosphate and carbonate precipitates in three intervals of solution pH, (i.e., pH<8, 8>pH<11, and pH>11). From the three observations of lanthanum orthophosphate solubility in acidic solutions (see Table 38) the solubility parameter was estimated. A simple derivative type search was used to find this value. This parameter was found to decrease in value to -47.1 ± .16. The equilibrium program was modified to substitute the higher value for solutions in which the pH is less than or equal to 7. As wastewaters are usually basic, the higher estimate which was calculated from a large set of data (i.e., twelve experiments) will see greater use.

The model's predictions are compared to the experimental observations in Figures 9 to 13. The point values of the former group are presented by open circle and the interval by a straight line. The observed values by the open triangle. The following comments are made on the model's simulation of the experimental data.

Within the estimated 99 percent confidence interval ,the predicted lanthanum concentrations were in agreement in six out of nine cases. The remaining three cases were close to the error interval, being 1 to 3 mg/l away. The model also demonstrated the same trend as the data, the lanthanum residual concentration increasing with increasing solution pH.

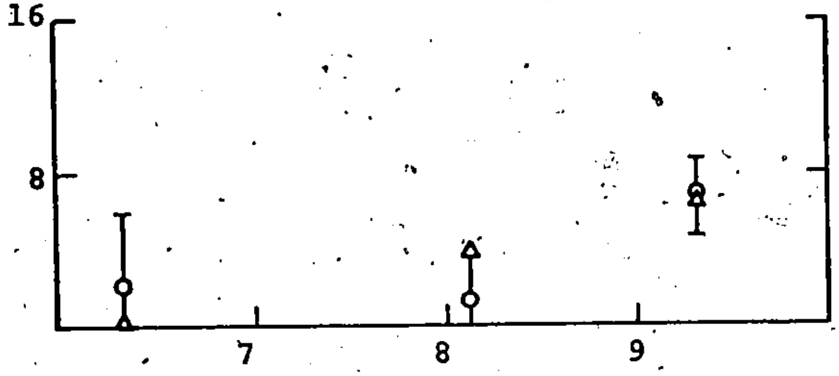
In five cases, the measured tripolyphosphate residual fell within the interval of the model's prediction. The particular region of discrepancy between the model and the experimental data is in those solutions in which the pH value is greater than 9. In this region, the model predicted no precipitation of tripolyphosphate. The complex, $LaP_3O_{10}^{-2}$, was calculated to be the dominant species among the soluble tripolyphosphate compounds at this bascity. In comparison, removals of 66 to 93 percent were observed. In the earlier experiments where precipitation of only tripolyphosphate had been investigated (see section 2, Appendix IV), none of the solutions were at pH greater than 9. The experimental criterion had not favoured this experimental condition. Thus the solubility had not been evaluated with data obtained at this pH level.

In comparing the observed to predicted residual levels of orthophosphate, the model was found to fit well in the acid solutions. With the basic solutions, a large discrepancy was found between the values in three out of six cases. In these three cases, the deviation from the percent of orthophosphate observed to be removed, and that removal which is ideally possible was from 30 to 50 percent. The percent which can be ideally removed is assumed equal to the percent of the stoichiometric requirement of lanthanum initially available. This requirement can be derived from the charge balance of the lanthanum cation and all of the phosphorus ion components. Looking back to the experiments of the single phosphate system (see section 1, Appendix IV), the observed percent removal was never less than 12 percent from that removal which is ideally possible. Thus, in these three cases, the observed removal is not in agreement with the ones observed in the simpler systems. This discrepancy is believed to have resulted from the experimental techniques. The poor removal observed in the last set of experiments is believed to be due to the failure of the membrane filter to remove all of the colloidal particles. This view is taken, as it had been observed that the solid phases in the alkaline solutions did not form distinctive floc

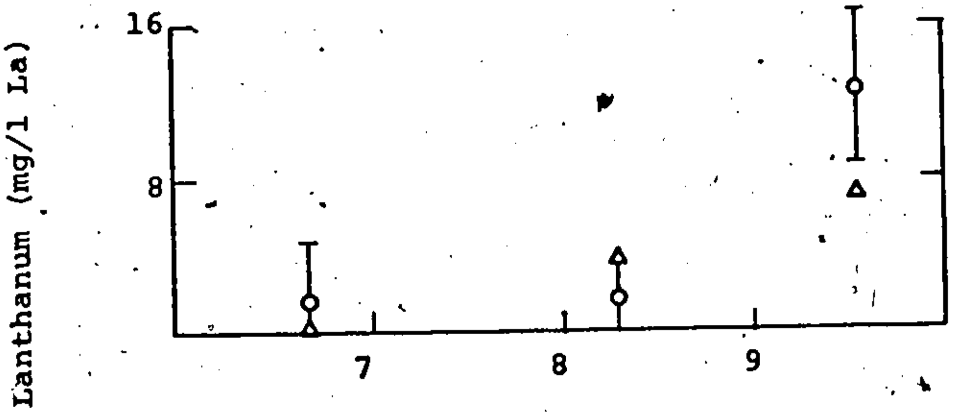
LANTHANUM RESIDUAL DISTILLED WATER

FIGURE 9

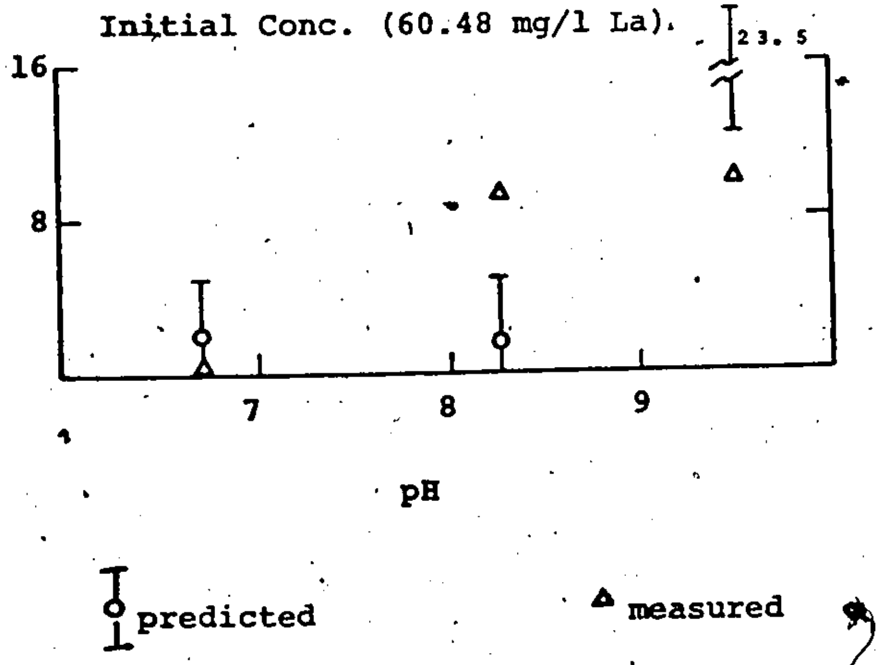
Initial Conc. (75.6 mg/l La)



Initial Conc. (68 mg/l La)

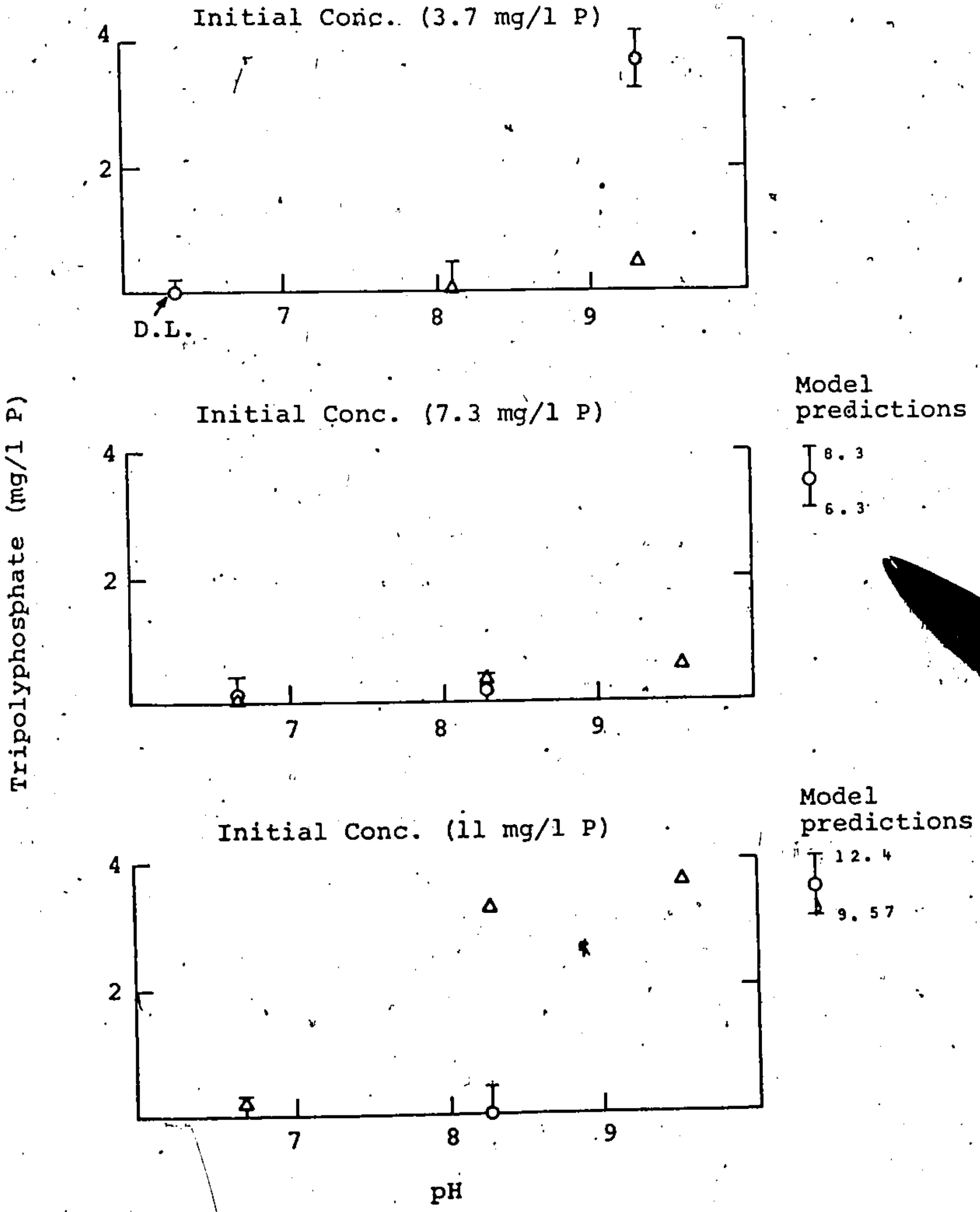


Initial Conc. (60.48 mg/l La)



TRIPOLYPHOSPHATE RESIDUAL DISTILLED WATER

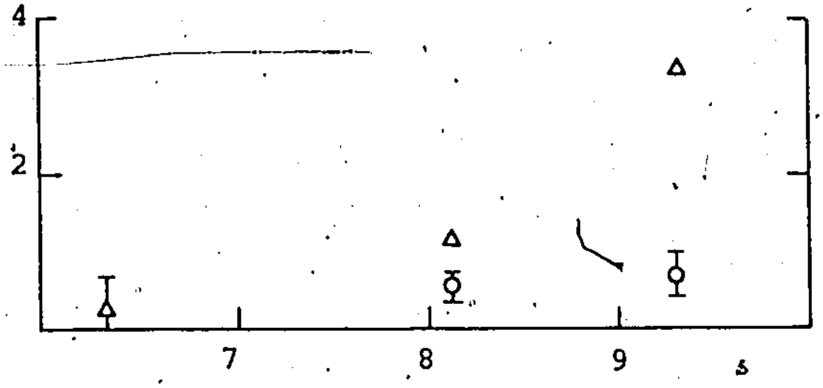
FIGURE 10



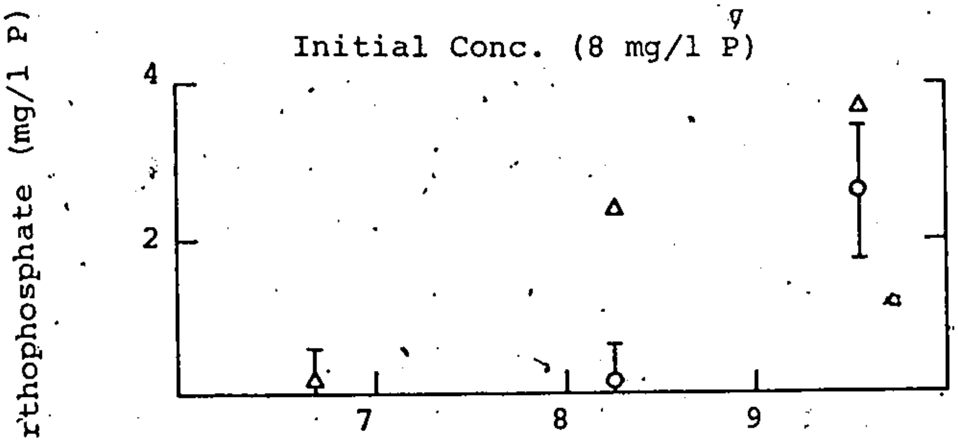
ORTHOPHOSPHATE RESIDUAL DISTILLED WATER

FIGURE 11

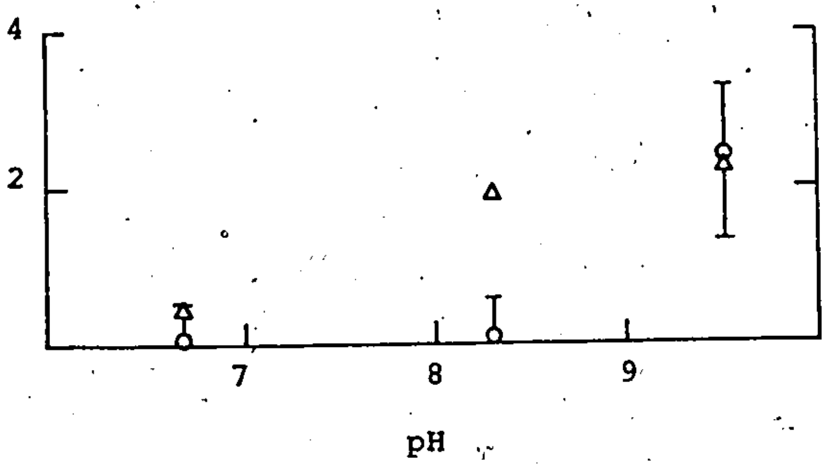
Initial Conc. (12 mg/l P)



Initial Conc. (8 mg/l P)

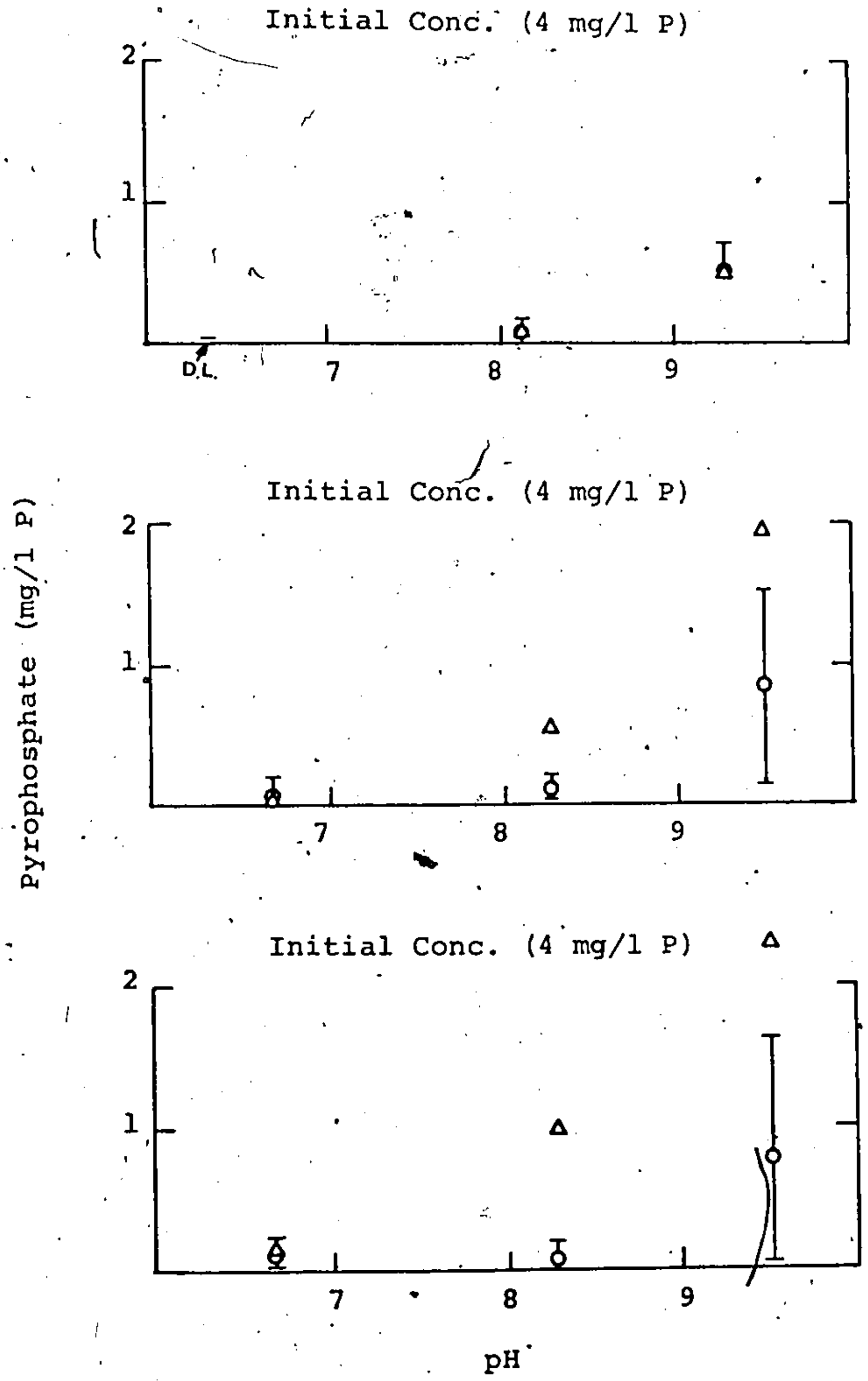


Initial Conc. (4 mg/l P)



PYROPHOSPHATE DISTILLED WATER

FIGURE 12



Initial Conc. (4 mg/l P)

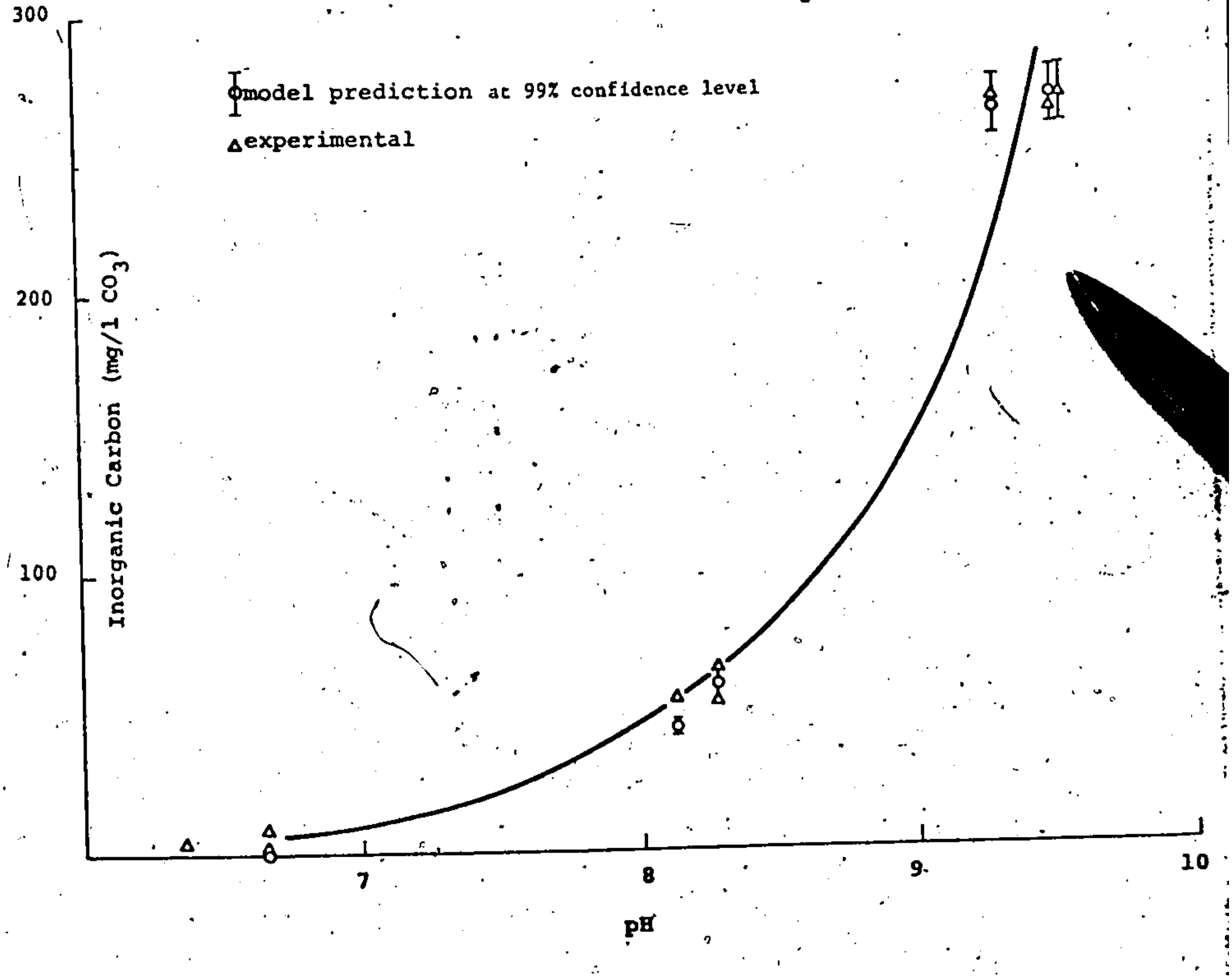
Initial Conc. (4 mg/l P)

Initial Conc. (4 mg/l P)

CARBONATE RESIDUAL DISTILLED WATER

FIGURE 13

Initial Conc. (240.1 mg/l CO_3)



particles, but rather dispersions.

With respect to the pyrophosphate residual concentration, the computer model and experimental values were in agreement with the general trend. This trend indicated a decrease in pyrophosphate removal with respect to increasing solution pH. This decreasing removal resulted from the increasing dominance of the $LaP_2O_7^{-1}$ complex as the anion disocciated from hydrogen to a greater extent in basic solutions.

In Figure.13, it is seen that the prediction of the residual total carbonate concentrations are similar to those observed.

V.2 Phosphate Removal in Wastewater

The equilibrium model of phosphate precipitation in distilled water was modified by the addition of three chemical components, calcium, magnesium, and sulphate and the twenty-three species which they form. These species which consist of ion complexes and precipitates increase the set of reaction equations to fifty. A listing of the components, species, reactions and free energy parameters are reported in Table 45 of section 2, Appendix V.

The free energy parameters for the sulphate, calcium, and magnesium complexes were taken from the literature sources listed in section 10, Appendix I.

The selection of the calcium precipitates was based upon the investigation of McCarty and Ferguson (F-2). From these studies in synthetic and actual sewage they observed the following precipitates:

(i) hydroxapatite,
(ii) calcite,
(iii) magnesium calcium carbonate (97% calcium, 3% magnesium),
(iv) β-tricalcium phosphate,
(v) brucite.

They had estimated a set of solubility parameters for these salts, but these estimates were dependent upon the solution pH, molar ratios of calcium to carbonate and calcium to magnesium. Different combinations of these solid phases with their respective solubility parameters were tested in the computer model. From this set, the hydroxyapatite and magnesium calcium carbonate precipitates were chosen on the basis of providing predictions of the soluble calcium and carbonate concentrations which were closest to the observed values.

The reaction which results in the calcium pyrophosphate precipitate was also tested in the computer model. The solubility parameter for this salt has been reported by Stumm and Morgan (S-14). A negligible amount of this precipitate was found to have been formed, and therefore the species was removed from the model. No evidence of a calcium tripolyphosphate precipitate was found in the literature. Also, the experiments carried out by Cronin (C-4) showed no evidence of the precipitation of the condensed phosphate with calcium from wastewater when the orthophosphate ion was not present.

Except for one reaction, the free energy parameters for the lanthanum precipitates and the lanthanum condensed phosphate complexes were estimated from the experiments of each phosphate species reacting by itself in distilled water, (see sections 2 to 4, Chapter IV). In acidic solutions, the solubility parameter of the lanthanum orthophosphate precipitate was determined from the three experiments in which both the ortho- and condensed phosphates precipitated from solution. The manner in which this parameter was calculated is discussed in the previous section.

An error interval was calculated along with each point value as had been done with the distilled water model. This interval was estimated at the 99 percent confidence level with the same Student's t ratio as before and estimates of the effective errors in the model predictions calculated from equation (20), (see section 3, Chapter III). The parameter covariance matrix, Covar (B), was expanded to a dimension of sixteen by the addition of error estimates reported with the free energy parameter estimates of the calcium and magnesium condensed phosphate complexes. This matrix is reported in Table 46 of section 2, Appendix V. Similarly the variance matrix Covar (X_u) was also expanded to include the initial components. The error estimates are reported in Table 47 section 2, Appendix V. The errors estimated for the components lanthanum, tri-, pyro-, and orthophosphate were based upon errors in stock solutions, volumes of aliquots, and the final dilution volume as before. The errors in the components sulphate, calcium, magnesium, and carbonate which were already present in the sewage samples were estimated from errors in their analyses. The errors in measured quantities were taken from the same sources as in the distilled water model. The error in the calcium analysis was based upon experience with this technique and its estimate reported in section 7 of Appendix IV. The major contributor to the effective error was found to be the errors in the initial concentrations of the components.

The predictions of the equilibrium model are compared to the experimental observations in Figures 14 to 19. Comments for each type of response follows.

The agreement in prediction of the residual lanthanum concentration is good in all cases. Though the error interval estimate for the residual concentration in acidic solutions was large, the predicted concentration is remarkably close to that observed.

The tripolyphosphate predictions are also excellent. The differences between the predicted and observed values that occurs, in distilled water solutions of pH > 9 is not seen here for solutions of pH $\approx$ 8.5. This indicates that the model predictions with respect to the tripolyphosphate residual concentration are valid in solutions whose pH approaches 9.

The experimental orthophosphate residuals fall within the error estimates in six cases, are extremely close in the other two, and differ only by 1.2 mg/l in one case. The measured residual shows a slight minimum at the neutral pH level, while the model shows a slight maximum. This results from the use of two parameter estimates for the lanthanum orthophosphate solubility at different pH levels. The magnitude of these trends is, however, slight, especially in comparison to the magnitude and uncertainty attached to these estimates.

The pyrophosphate responses are in good agreement in all nine cases.

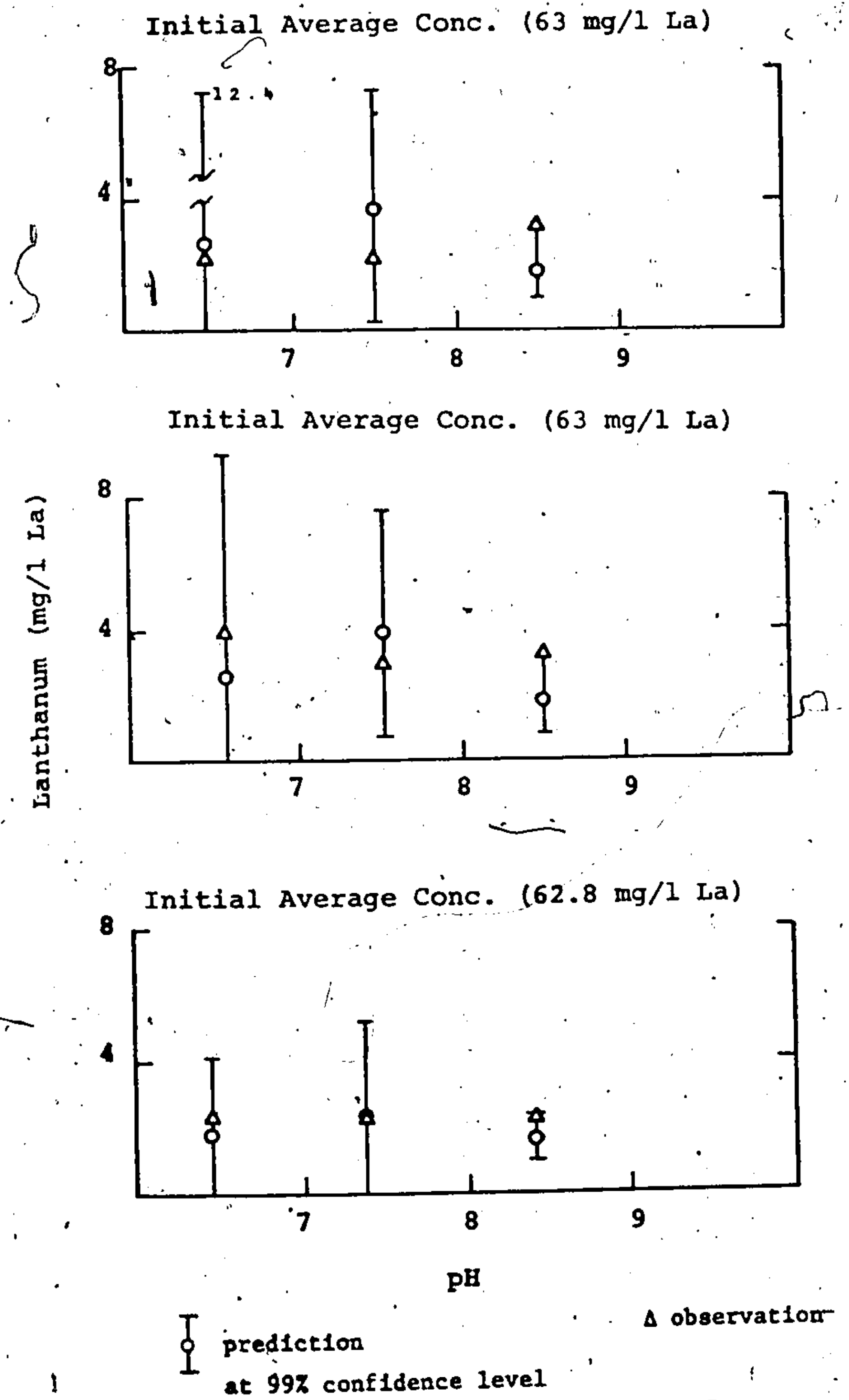
The prediction of the calcium residual differs significantly from the observed values in only one case. This deviation is a result of the prediction of more calcium carbonate being formed in the solid phase than actually existed.

The model is seen to consistently predict less carbonate remaining in solution at pH ≈ 8.5, than observed. An explanation for this occurrance may be that a carbonate complex which is effective at this pH level has not been included. A cation which has not already been considered for this reaction is however unknown.

In summary, it is felt that the agreement between the six sets of predictions and observations (fifty-four values in all) indicates that the computer model adequately simulates the precipitation of phosphates with lanthanum at a metastable state. It is significant that this success was achieved by considering only a select number of inorganic components.

LANTHANUM RESIDUAL WASTEWATER

FIGURE 14

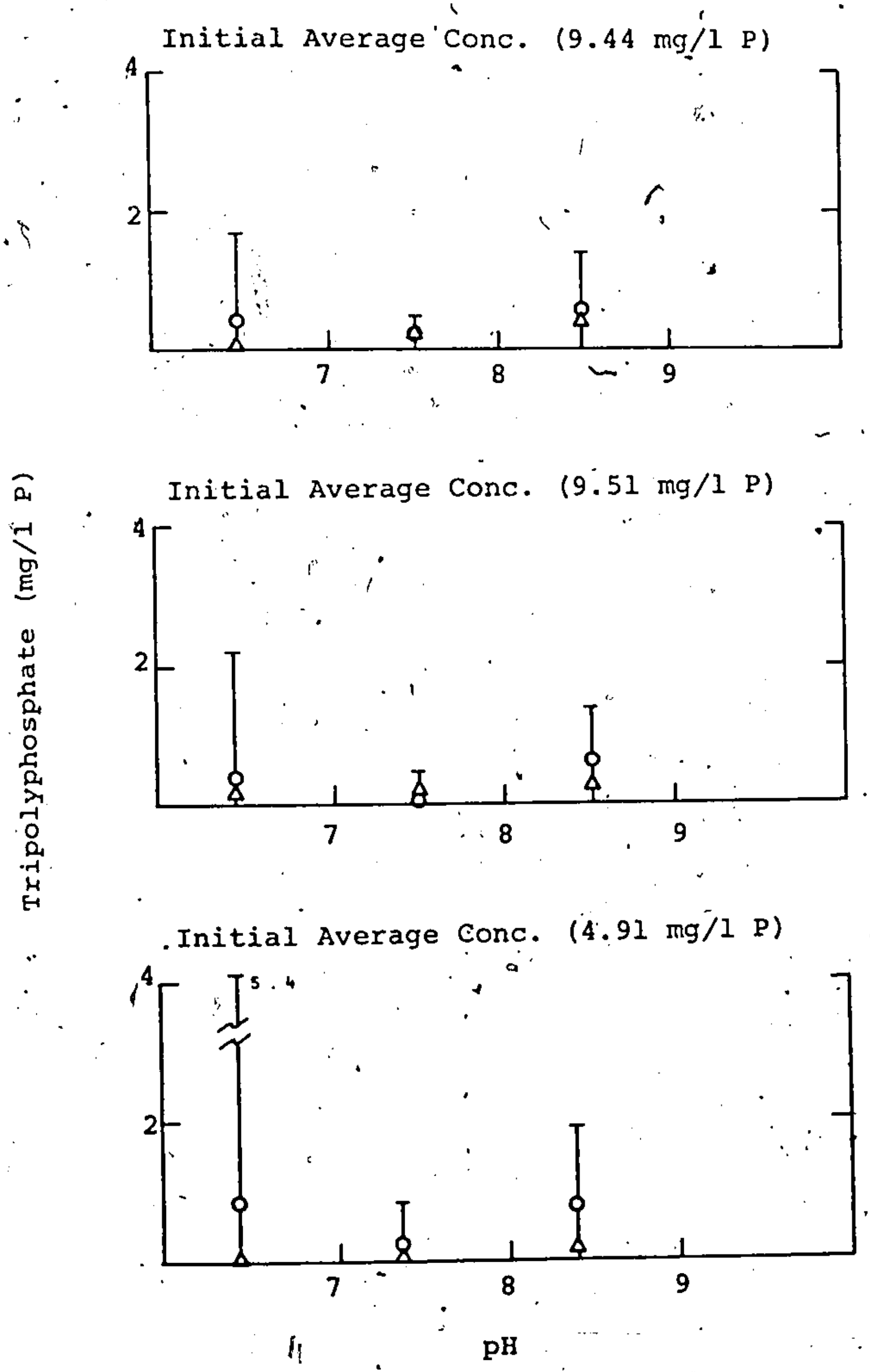

Initial Average Conc. (63 mg/l La)

Initial Average Conc. (63 mg/l La)

Initial Average Conc. (62.8 mg/l La)

TRIPOLYPHOSPHATE RESIDUAL/ WASTEWATER

FIGURE 15

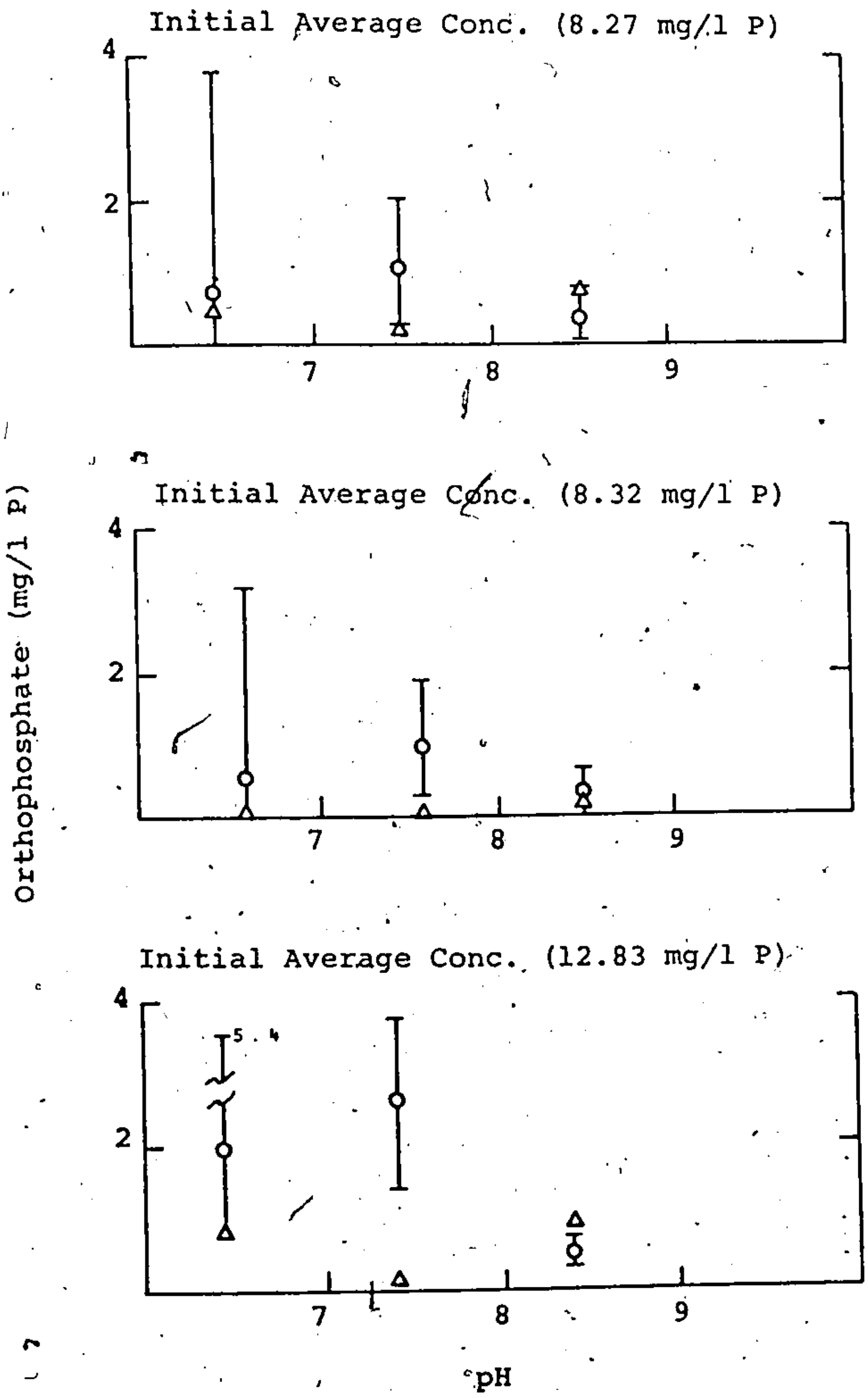

Initial Average Conc. (9.44 mg/l P)

Initial Average Conc. (9.51 mg/l P)

Initial Average Conc. (4.91 mg/l P)

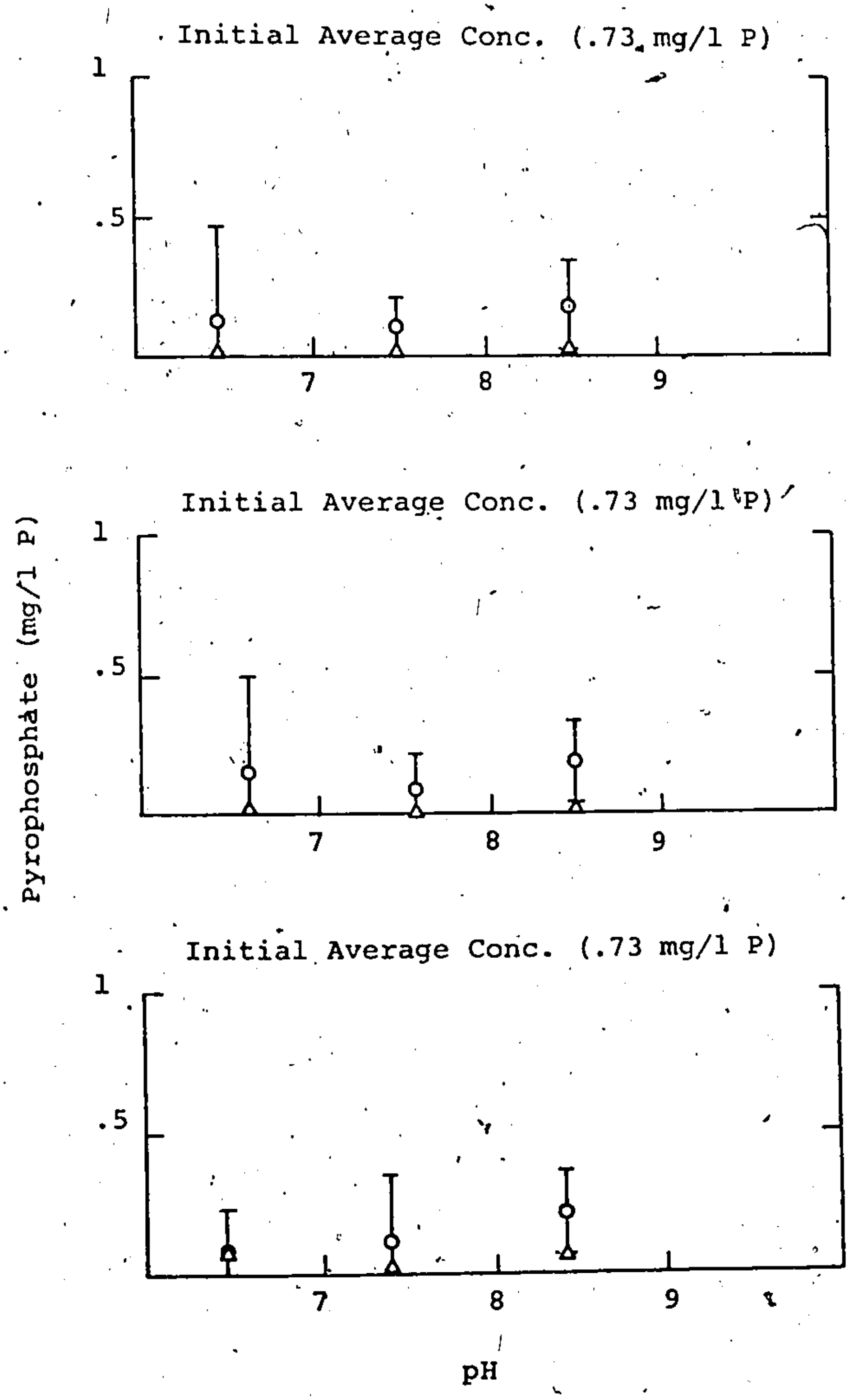
ORTHOPHOSPHATE RESIDUAL WASTEWATER

FIGURE 16



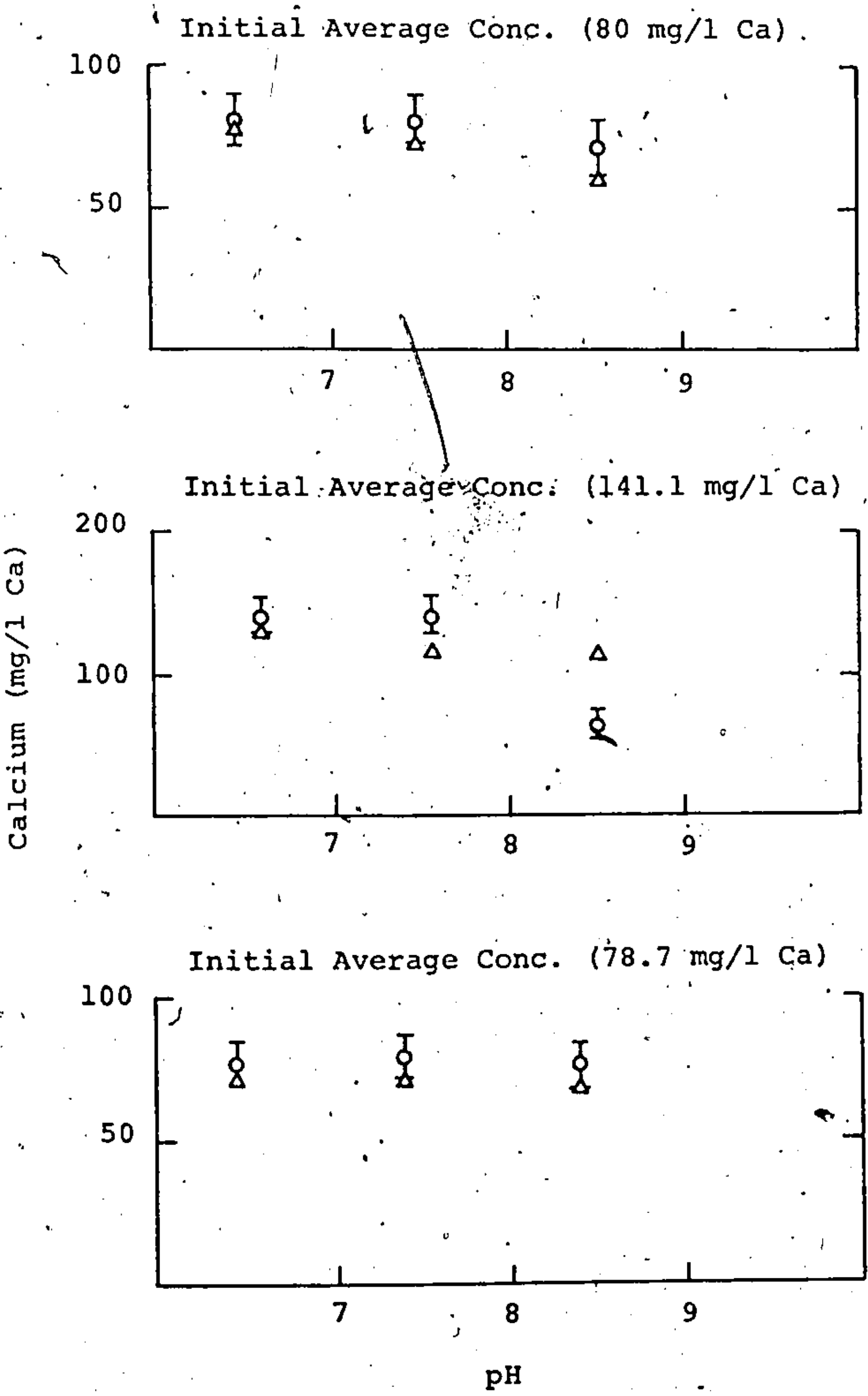
PYROPHOSPHATE RESIDUAL   WASTEWATER

FIGURE 17



CALCIUM RESIDUAL WASTEWATER

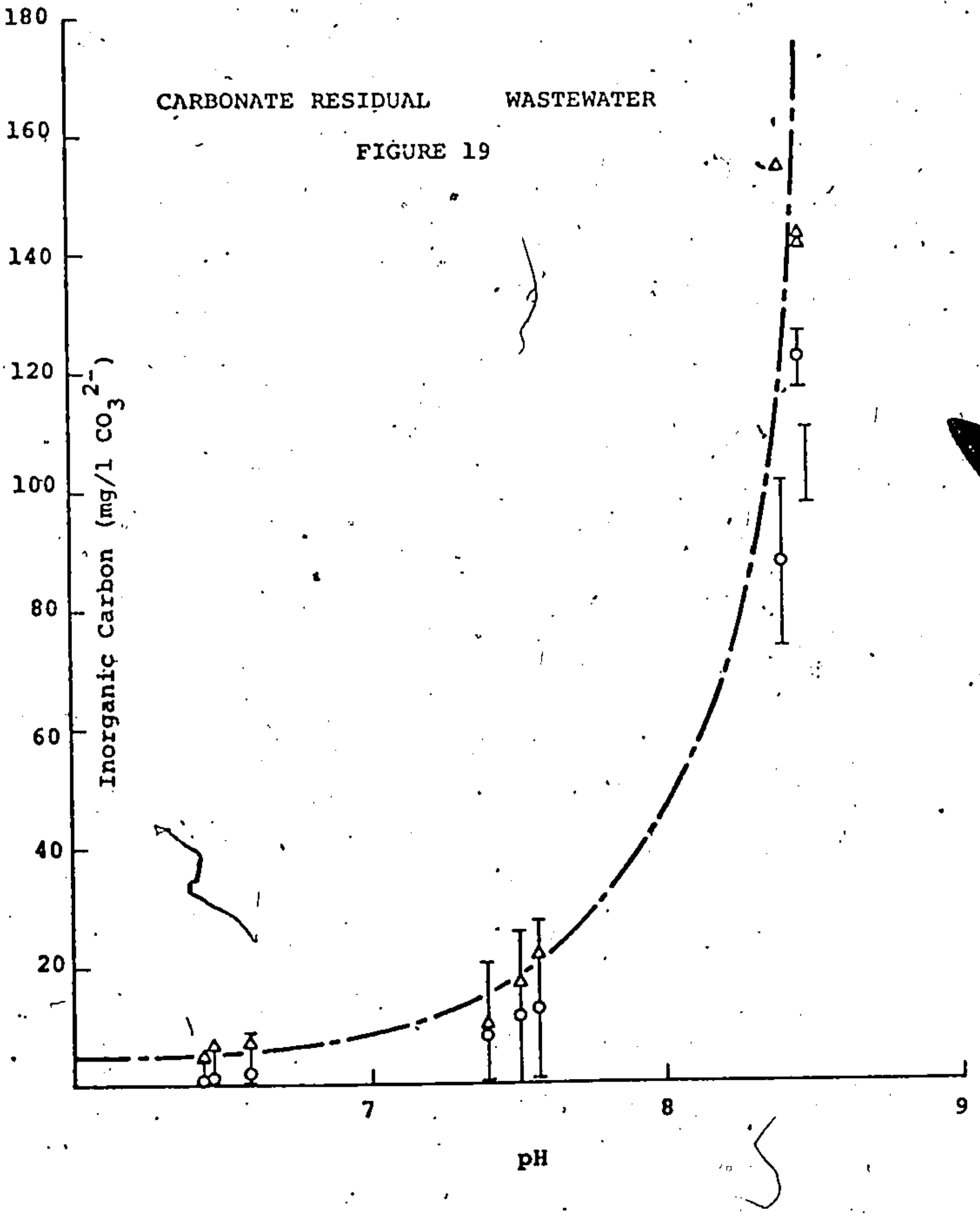
FIGURE 18



Initial Average Conc. (80 mg/l Ca)

Initial Average Conc. (141.1 mg/l Ca)

Initial Average Conc. (78.7 mg/l Ca)



CARBONATE RESIDUAL WASTEWATER

FIGURE 19

No organic species have been considered. This is due in part to the inability to characterize conveniently the number and diversity of compounds. On a routine basis, this organic fraction in sewage is characterized as the total concentration of carbon and recently by distributions of molecular weights. The computer model will now be turned about to predict the lanthanum dosage needed to meet a specific residual level of phosphates.

V.3 Lanthanum Dosage Model

Until now, the calculation of the equilibrium composition had been approached in a conventional manner. The initial aqueous concentrations of the components were specified and the equilibrium composition then calculated. In the dosage model, this procedure has been amended. Some of the initial component concentrations along with certain conditions at equilibrium are now set. The total residual phosphate concentration and solution pH are the variables of the latter group. The lanthanum dosage and the remaining portion of the equilibrium composition are then determined.

The set of reactions, components, and species used in this model are the same used in the previous wastewater model with one exception (see Table 45). The component potassium and its related species have been removed. This component has a negligible effect on dosage requirements.

As before, the "CHEMIST" subroutines formed the basis in the solution of the complex chemical equilibria problem. The main program "TST" converted the concentration units of the input data and directed the search for the required lanthanum dosage. Two new subroutines, "TAB" and "EXPER", were added and "MODEL" modified.

The initial composition of a wastewater sample is expressed by the concentration of the following inorganic components:

(i) ortho-, tripoly-, and pyrophosphate (mg P/1),

(ii) hardness as represented by the calcium and magnesium ion concentrations (mg $MeCO_3$/1),

(iii) alkalinity expressed as the total inorganic carbon concentration (mg CO_3/1),

(iv) sulphate ion concentration (mg SO_4^{-2}/1),

(v) chloride ion concentration (mg Cl^-/1),

(vi) sodium ion concentration (mg Na^+/1),

(vii) solution pH.

The equilibrium rather than initial pH is specified. The required value is achieved by the addition of acid and base to the chemical system. The initial pH was not chosen as a parameter because the buffer capacity of wastewater is underestimated by the set of chemical components used here. Though, the buffering capacity of the carbon dioxide-carbonate equilibrium is included in the model and provides a significant contribution, it is not enough. The additional capacity may arise from organic species not considered. Included with the input quantities are their estimated standard deviations with the exception of sodium, chloride and pH.

The search technique first used to estimate the lanthanum dosage was based upon the Newton Raphson method. The partial derivative of the total residual phosphate concentration with respect to the lanthanum dosage was calculated as the sum of the partial derivatives of the separate phosphate species. The increment of lanthanum to be added to the system at each iteration is determined from the product of the deviation between the present and specified equilibrium levels and the reciprocal of this derivative. The method appeared feasible. If the dosage is overspecified, the method is to recover by calculating a negative increment for the next cycle. In practice, the method converged slowly because the correct value was continually being overshot. This failure is a result of the non-linearity of the relationship between lanthanum dosage and phosphate residual. The convergence problem was solved by the use of a second method called "Regula Falsi" (C-6).

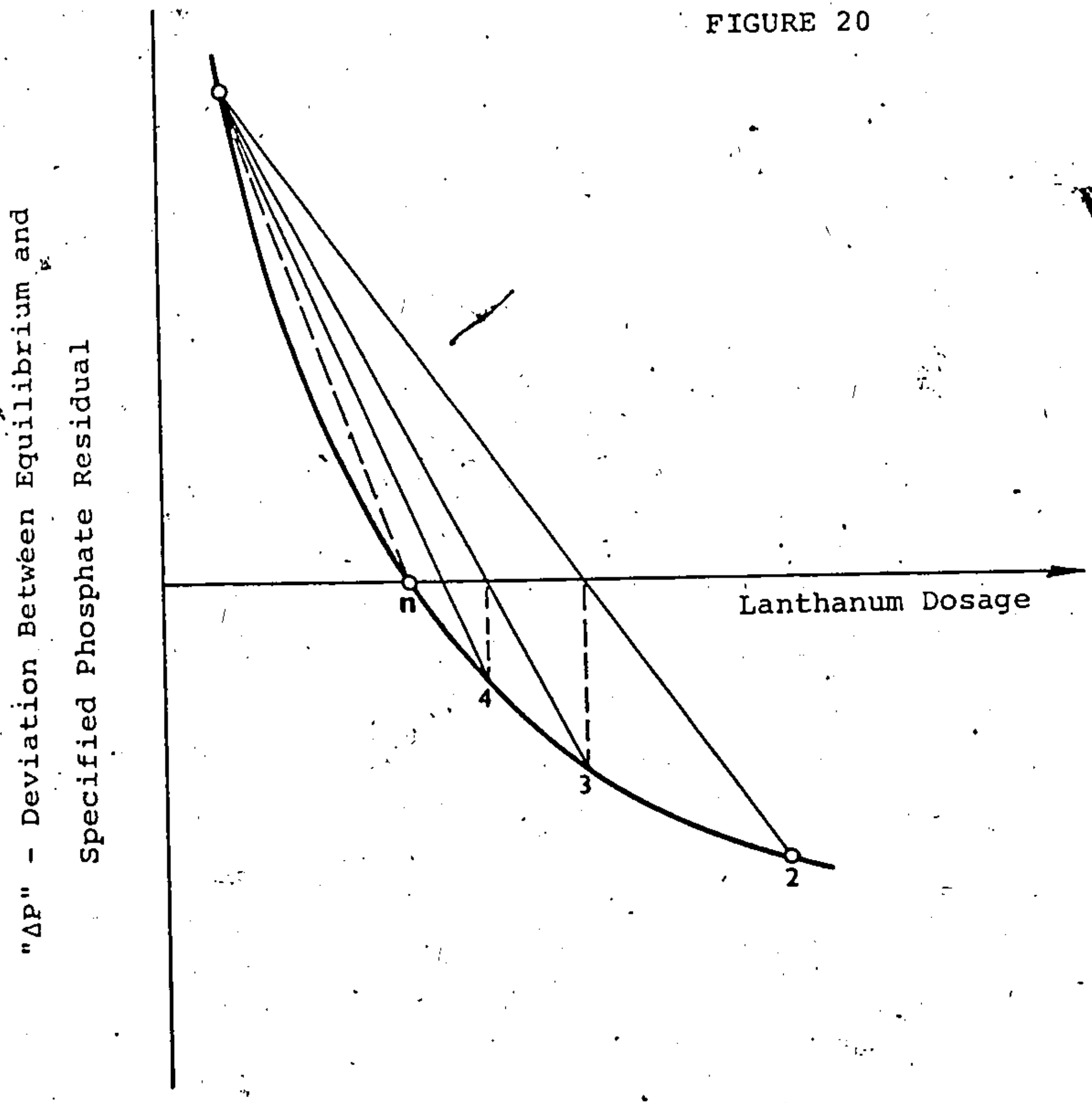
The search is initiated by using 90 percent of the stoichiometric requirement of lanthanum as an initial quess. The Newton Raphson procedure is used until overshoot occurs (i.e., the lanthanum dosage is overspecified). The required dosage lies between the last two estimates. These values are used to start the "Regula Falsi" search. This method is best explained by looking to Figure 20. The difference between the equilibrium and required total phosphate concentration is plotted as a function of the lanthanum dosage. A unique characteristic can be expected for each wastewater sample. The last estimates (point 1 and 2) lie above and below the abscissa (overshoot) and the interval between these points is approximated by a chord to the curve. The next estimate (point 3) of dosage is taken as the intersection of this chord and the abscissa. Substituting this estimate into the model, a smaller deviation in the phosphorus concentrations results. A new chord is drawn, and the calculations repeated. At each iteration, the length of the chord decreased until one end (point n) coincided with the intersection of the curve and abscissa. This method was found to converge in all cases attempted.

An alternate choice is available at which level to set the residual phosphorus concentration. In the examples here the lanthanum dosage was calculated to provide a residual concentration of 1 mg P/l. This is in keeping with the present objectives of phosphate removal in the Great Lakes Basin (see section 2, Appendix I). A second choice utilizes error estimates. The residual concentration to be met is the upper limit of a confidence interval rather than the predicted value itself. This limit is calculated as the sum of the predicted level and the product of the effective error estimate (from equation (20)) and a Student's t value. This latter approach simulates the practice carried out by the Ministry of the Environment of Ontario in selecting a chemical dosage.

USE OF REGULA FALSI METHOD

TO ESTIMATE THE LANTHANUM DOSAGE

FIGURE 20



Because of its nature and source, the chemical properties of sewage can be expected to be highly variable, (section 3, Appendix 1). The problem is to determine the chemical dosage which would consistently provide the required removal of phosphates over a definite period of time. The Ministry's approach to this problem is to treat the changing quality of wastewater as a random occurrance and hence the removal observed for a particular chemical dosage, a random variable, (see section 4, Appendix I). This variable is assumed to be distributed normally. The procedure is to measure the residual phosphate concentrations which result from random samples of wastewater (at least ten) treated with different quantities of precipitant (usually at least three). The observations are plotted as the frequency of occurrance (normal probability scale) versus the residual concentrations. The measurements taken at each level of precipitant lie on a particular straight line. The intersection of one of these family of lines with a co-ordinate represents the removal needed, for example a residual concentration equal to or less than 1 mg P/1, 80 percent of the time.

This situation is simulated in the computer model by first representing the changing quality of wastewater by the magnitude of the errors associated with the input components. The frequency with which a residual phosphate concentration will be less than or equal to a required value is expressed by the confidence level chosen for the Student'st ratio. Thus the computer model and information about the variance of the inorganic components in wastewater can be substituted for the experimental method of selecting the amount of precipitant.

The main program "TST" in addition to processing data also prints out the equilibrium composition. Error estimates are included with the model's predictions. An example of this model's report of the initial and final quality of a wastewater is reported in Table 14.

The subroutine "MODEL" was modified in order that the specified pH at equilibrium be met for each solution. This is done by a call to the subroutine "PHSLV".

The utility subroutine "TAB" supplies the Student's t values for a range of confidence levels of 55 to 99.5 percent in 5 percent increments. These values are for 19 degrees of freedom, the minimum number available from the phosphate experiments described in Chapter IV. As only the upper limit is of concern, the confidence level and the fractional area of the Student's t distribution at which the ratio is evaluated are equivalent.

The error estimates included with the model's predictions are calculated by the subroutine "EXPER". The calculations are based upon equation (20). The parameter covariance matrix Covar (B) and estimates of the analytical errors are the same which were used in the wastewater model described in the previous section. The variance matrix of the independent variables Covar (X_u) is supplied from the data.

TABLE 14

SAMPLE INPUT - OUTPUT INFORMATION
FROM THE LANTHANUM DOSAGE MODEL

Initial Information on Water Quality

Phosphate Distribution	(MG-P/L)	Standard Deviation
Orthophosphate	1.000	.040
Pyrophosphate	1.000	.040
Polyphosphate	8.000	.320
Total Phosphate	10.000	

Hardness	(MG/L)	Standard Deviation
Calcium Carbonate	250.000	6.250
Magnegium Carbonate	65.000	1.800

Total Inorganic Carbon Concentration	(MG-CO3/L)	Standard Deviation
	250.000	3.500

Ion Concentration	(MG/L)
Sodium	162.000
Chloride	212.000
Sulphate	180.000

Final Solution PH 8.000

Predicted Water Quality of the Effluent

Required Lanthanum Dosage 29.080 (MG-LA+3/L)

Residual Lanthanum		Standard Deviation
	3.728	.627

Phosphate Distribution	(MG-P/L)	Standard Deviation
Orthophosphate	.570	.107
Pyrophosphate	.143	.030
Polyphosphate	.298	.118
Total Phosphate	1.011	.073

Hardness	(MG/L)	Standard Deviation
Calcium Carbonate	250.030	8.840
Magnesium Carbonate	65.002	2.425

Total Inorganic Carbon Concentration	(MG-CO3/L)	Standard Deviation
	35.798	6.605

Ion Concentration	(MG/L)
Sodium	212.000
Chloride	284.837
Sulphate	180.000

The errors in the initial concentrations are assumed to be independent. As the quantity of lanthanum is to be determined, no error is assigned to this component.

V.4 Sensitivity Analysis of the Dosage Model

Tests were carried out with the computer model to determine the sensitivity of the independent variables (i.e. the initial concentrations of the components) upon the quantities of precipitant required. A comparison of partial derivatives clearly indicated that the initial concentrations of phosphates were the most sensitive variables. The dependent variables of these derivatives are the predicted phosphate concentrations at equilibrium. Therefore three sets of experiments were selected in which the initial distribution of phosphate species is varied but the total concentration of phosphorus among the sets is held constant. This condition allows a comparison of the dosage requirements among sets. In each set, the computer model is tested at two levels of the six independent variables shown in Table 15. The sequence of values assigned to these variables is based upon a one eighth factorial design of the possible sixty-four combinations. The initial concentrations of sodium and chloride ions are treated as one variable. These components affect the model's predictions in the same manner through the ionic strength of the solution. The initial distribution of phosphates is reported in the following table.

TABLE 15

INITIAL CONCENTRATION OF COMPONENTS

Experiment Number	Calcium	Magnesium	Total Carbonate	Sodium	Chloride	Sulphate	pH
1	125 ± 3.13	33 ± .83	250 ± 3.5	162	212	180 ± 9.0	7
2	250 ± 6.25	33 ± .83	250 ± 3.5	81	106	90 ± 4.5	7
3	125 ± 3.13	65 ± 1.8	125 ± 1.7	81	106	180 ± 9.0	7
4	250 ± 6.25	65 ± 1.8	125 ± 1.7	162	212	90 ± 4.5	7
5	125 ± 3.13	33 ± .83	125 ± 1.7	162	212	90 ± .45	8
6	250 ± 6.25	33 ± .83	125 ± 1.7	81	106	180 ± 9.0	8
7	125 ± 3.13	65 ± 1.8	250 ± 3.5	81	106	90 ± 4.5	8
8	250 ± 6.25	65 ± 1.8	250 ± 3.5	162	212	180 ± 9.0	8

TABLE 16

INITIAL PHOSPHATE CONCENTRATIONS

Component	Set A	Set B (mg P/l)	Set C
Orthophosphate	4.5 ± .18	8 ± .32	1 ± .04
Pyrophosphate	1 ± .04	1 ± .04	1 ± .04
Tripolyphosphate	4.5 ± .18	1 ± .04	8 ± .32
Total	10	10	10

The lanthanum dosage was calculated on the basis of providing a total residual phosphate concentration of 1 mg P/l. The alternative criterion which is the upper limit of a confidence interval was not chosen because the estimated standard error of the total phosphate concentration was found to be correlated with pH. This is shown in the next table. The major contribution to this error estimate is from the uncertainties in the initial concentrations of the components (i.e., Covar (X_u) of equation (20)). It does not arise from the situation where the lanthanum orthophosphate solubility parameter used for solutions at pH 7 was estimated from a smaller number of observations than the other parameters, and thus is less precisely known.

TABLE 17

ESTIMATED STANDARD DEVIATION OF TOTAL RESIDUAL PHOSPHATE CONCENTRATION

pH Level	Set A	Set B	Set C
7	0.49	.51	0.47
8	0.16	.21	0.17

The lanthanum dosages and residual aqueous concentrations are reported in Table 18. The influence of each parameter is determined by subtracting the sum of responses found at the low level from the sum of the higher level and dividing by N/2 (where N is the number of experiments). This procedure is suggested by Box and Hunter (B-17). As only a fraction of the possible experiments were carried out, the second order effects (i.e., the mutual influence of two parameters) is confounded with the first (i.e., the parameter itself). In a screening experiment, such as here, the second order effects are neglected. The parameters with the magnitude of their effects are reported in decreasing magnitude in Table 19 for each set.

From Table 18, it is evident that the variation between sets of the dosage requirements is greater than the variation within a set. This confirms the original assumption that the phosphate species are the most sensitive of the input parameters. These average dosage values also indicate that

TABLE 18

LANTHANUM DOSAGE AND RESIDUAL CONCENTRATIONS

Expt. No.	Set A Dosage	Set A Residual	Set B Dosage (mgLa/l)	Set B Residual	Set C Dosage	Set C Residual
1	34.5	2.32 ± .78	40.78	2.37 ± .84	28.29	2.32 ± .78
2	34.07	1.86 ± .57	40.30	1.91 ± .61	27.85	1.86 ± .56
3	34.53	2.31 ± .53	40.77	2.33 ± .60	28.31	2.31 ± .53
4	33.46	1.27 ± .24	40.56	2.12 ± .52	28.15	2.10 ± .46
5	33.92	2.33 ± .41	40.14	2.33 ± .51	27.77	2.39 ± .41
6	34.88	3.32 ± .56	41.09	3.32 ± .72	25.38	1.99 ± .51
7	33.89	2.29 ± .42	40.11	2.29 ± .52	27.68	2.3 ± .41
8	35.31	3.72 ± .64	41.55	3.74 ± .81	29.08	3.73 ± .63
Average	34.07	2.34	40.66	2.55	27.81	2.38

the lanthanum requirements decrease with the increase in percent of tripolyphosphate present. This results from the removal of 1.8 moles of phosphate for every mole of lanthanum when the condensed species are precipitated, as compared to the removal of 1 mole for the orthophosphate salt. A different trend was observed for the aqueous lanthanum concentration. Less variation is seen among the average values per set than the variation within any set. In the latter case, the residual concentration is observed to change by as much as 100 percent. With respect to this residual concentration, the nature and distribution of the phosphate species have little effect. No uniform order of the parameters with respect to sensitivity appears evident in examining Table 19 for either the dosage or residual lanthanum concentration.

The results of this study indicate that the complexity of a computer model (i.e., the number of components and reactions considered) is determined by the design parameters. If one wishes to predict, only the dosage requirements, then the phosphate species are the principal model components. The remaining water quality parameters may be removed in the interest of simplicity. This design requirement can arise in the case where chemical treatment is used on a "once-thru" basis. In a removal process using lanthanum, however, the chemical precipitant is recycled in order that the process is economically feasible, (see section 7, Appendix I). The residual concentration represents chemical losses in the

TABLE 19

PARAMETER EFFECTS *

Response	Set A Dosage	Set A Residual	Set B Dosage	Set B Residual	Set C Dosage	Set C Residual
	Sulphate 3.88	Sulphate 3.92	Sulphate 3.08	Sulphate 3.11	Sodium & Chloride 4.05	Sodium & Chloride 2.08
	pH 1.44	pH 3.90	Calcium 1.70	pH -2.95	Magnesium 3.91	Magnesium 1.88
	Carbonate .98	Carbonate .96	Sodium & Chloride .76	Calcium 1.77	CO_3 3.31	pH 1.82
	Calcium .85	Calcium .92	Carbonate -.71	Sodium & Chloride .71	pH -2.67	Sulphate 1.7
	Magnesium -.18	Magnesium -.24	Magnesium .68	Magnesium .55	Calcium -1.61	Carbonate 1.42
	Sodium & Chloride -.18	Sodium & Chloride -.14	pH -.48	Carbonate .21	Sulphate .37	Calcium .36

* (X no. of experiments/2)

recycle process, and thus is a design parameter. The complexity of the present model is justified for the recovery process.

As seen in Table 17, the uncertainty in the predictions of the residual phosphorus concentrations is greater in neutral solutions compared to basic ones. This results in part from the partial derivatives (Z_u) of the equilibrium phosphate concentrations taken with respect to the initial components being 20 to 50 percent higher when evaluated at a neutral pH. These derivatives are directly proportional to the error estimates (see equation (20)). Just as the computer model simulates an increased sensitivity of the components at pH 7, a corresponding situation may occur in the actual chemical system. The concentrations of the chemical components in wastewater can be expected to change continually. Therefore, the calculations from the computer model suggests it would be an advantage to carry-out precipitation in a basic solution to lessen the sensitivity of influent composition. The sensitivity analysis showed that changing this operating condition has a slight influence on the dosage. This observation shows that factors other than the minimum dosage requirement can influence the choice of operating conditions in a treatment process.

The predictions from the computer model can be used to estimate the operating costs of a treatment process. From Table 18, the maximum and minimum losses of lanthanum (i.e., residual aqueous concentrations) and dosages were observed to be:

(i) 3.74 to 1.27 mg La/l,

(ii) 41.6 to 25.4 mg La/l.

The cost of a mixed salt of rare earths (see Table 24, section 5, Appendix I) is quoted by the Molybdendum Corporation of America (M-13) at 37¢/lb. Assuming that the other rare earth phosphates are as equally insoluble as the lanthanum salts, the range of operating costs to replace chemicals lost to the effluent is from 1.2¢ to 3.5¢ per 1000 gallons sewage treated. This may be compared to a range of costs from 3.4¢ to 6.3¢ per 1000 gallons which result when lime, alum, or ferric salts are used to precipitate phosphates (K-7). The initial cost for a chemical inventory of lanthanum salts is from 24¢ to 39.5¢ per 1000 gallons. As noted previously in section 7 of Appendix I, the cost of recovering the lanthanum precipitate is approximately 7¢ per 1000 gallons compared to the cost of disposing the lime, alum and ferric precipitate which range from 3.7¢ to 5.3¢ per 1000 gallons. Therefore, the use of lanthanum as an alternative precipitant is economically viable.

This result strongly suggests that, in view of the advantages which lanthanum offers as a phosphate precipitant, further trials at the pilot plant scale (approximately 2500 gal/day) on a typical sewage influent should be carried out. Because of the variability in wastewater quality, a trial period of at least 90 days is recommended. As a preliminary step, the effectiveness of the rare earth mixed salts as a phosphate precipitant compared to the reagent grade lanthanum salt used here should be determined.

VI CONCLUSIONS

Lanthanum has been found to be highly effective as a precipitant of ortho- and condensed phosphates. When this cation is added in quantities sufficient to meet the stoichiometric requirements of the normal phosphate salts, a total residual phosphorus concentration of less tham 1 mg/l P (i.e., the present objective) is achieved. This performance is obtained over a wide range of solution pH from approximately 6.5 to 8.5.

It has been demonstrated that the solubility of the amorphous precipitates of lanthanum phosphate, hydroxide and carbonate can be described quite well by the solubility product concept. Solubility parameters were estimated for these precipitates and stability constants for certain lanthanum condensed-phosphate ion complexes from experimental observations. The precipitation of each phosphate species (i.e., ortho-, pyro-, and tripolyphosphate) with lanthanum from distilled water had been investigated separately. Because the solubility of these salts could only be characterized, by the total aqueous concentrations of lanthanum, phosphates, and carbonate (in certain cases), it was necessary to use an equilibrium model of each system to relate the experimental observations to the solubility and stability parameters. Estimates of these parameters were determined by application of the maximum likelihood principle to the measured responses. Multiple correlation coefficients greater than 0.99 were obtained for models of all three systems.

The solubility parameters estimated here indicate that the amorphous precipitates are more soluble than had been indicated previously in the literature. This is believed to be due to the lack of a well defined crystalline structure. Also, a change in solution temperature from 25 to 5°C was found to have slight influence upon the solubility of most precipitates.

Solubility and stability constants estimated from the same set of data were found to be highly correlated, though experiments had been designed to minimize the uncertainty associated with parameter estimates. The criterion used to design these experiments proved to be a useful guide in indicating when the return of information from further experiments became minimal.

From analyses of sewage influents sampled in the local area, it was concluded that ortho- and tripolyphosphate were the major phosphate constituents, and pyrophosphate a minor one. Estimates of the first order rate constants for the hydrolysis of these condensed phosphates showed that pyrophosphate would remain the minor constituent during wastewater treatment.

An equilibrium model has been written to predict the aqueous composition of a wastewater after treatment with lanthanum. The parameters in this model included both the estimates reported above and information from the literature concerning other reactions. This computer model accounts for the reactions of twelve major inorganic components found in wastewater which react to form forty-eight species in the gaseous, liquid and solid phases. The model's predictions were verified by comparison to nine sets of measurements taken of the wastewater composition after treatment with lanthanum. In the large majority of cases, the experimental observations lied within intervals predicted by the model. These intervals reflect the uncertainties in the parameter estimates, analyses, and experimental conditions. The model was turned about in order to calculate the lanthanum dosage necessary to obtain a specific residual phosphorus concentration given the initial wastewater quality.

This dosage model has been demonstrated as a useful tool in analyzing a treatment process. From a sensitivity analysis of the independent variables *(i.e., wastewater quality) it was concluded that the initial concentrations and distributions of phosphates have the greater influence in determining the chemical dosage. Conversely, the residual aqueous concentration was found to be more affected by those variables other than phosphates. Thus, the number of reactions which need be included in the equilibrium model is determined in part whether information about the residual

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*The residual phosphorus concentration in this analysis was aqueous concentration or dosage is sought. The computer model also indicates intervals over which the value of a particular variable (e.g., pH) strongly influences the final aqueous composition. These regions are to be avoided in a treatment process if this variable is expected to change continuously.

It has been demonstrated that the computer model is accurate when the independent variables, (e.g. initial composition and final pH) have values which lie with the region covered by actual experiments. This region is defined approximately as the initial concentrations of the major components being at millimole levels, and the final solution pH lying between 6 to 9. This restriction exists because the free energy parameters for the precipitates were not measured under conditions of true chemical equilibrium but rather at conditions similar to the actual treatment process. Therefore, these parameters cannot be considered to represent equilibrium constants. The objective of this work, (i.e. to simulate the chemical treatment for phosphorus removal) has, however, been met.

Finally, from the information calculated with the computer model, the range of costs associated with lanthanum treatment is estimated. These cost estimates based upon this study and other investigations reveal that it is economically feasible to substitute lanthanum with its recovery process in place of conventional phosphate precipitants which are used only once and then disposed. This conclusion along with the superior properties of lanthanum as a precipitate

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LIST OF MATHEMATICAL SYMBOLS

FOR CHAPTERS 1 - 6

a_ℓ	activity of species i
$a_{\ell i}$	stoichiometric coefficients
B_ℓ	number of moles of components
C_i	Free Energy parameter of species i
D_1	Experimental Design Criteria
D_2	
D_3	
e_{iu}	prime error of i-th observation in the u-th experiment
F_i	Gibbs Free Energy of species i
K_i	Equilibrium constant for species i
N_i	model of i-th observation
R	universal gas constant
T	temperature (degrees Kelvin)
V_{ij}	products of the residuals between the observations and model predictions
x_i	number of moles of species i
$\hat{X}_\ell$	mole fraction of species i
X_k	total number of moles in compartment k
Y_{iu}	observation i in the u-th experiment

β	vector of model parameters
W_i	matrix of partial derivatives of the i-response taken with respect to the model parameters
X_u	vector of independent variables for the u-th experiment
Z_i^u	partial derivatives of the i-th response with respect to u-th experiment
ε_{ju}	prime error of i-th observation in u-th experiment
γ_i	activity coefficient of species i
σ_{ij}^u	covariance of the i-th and j-th observation in the u-th experiment

APPENDIX I: BACKGROUND

I.I EUTROPHICATION AND THE ROLE OF PHOSPHORUS

Phosphorus is an essential nutrient to all life systems on earth. The basic component, the biological cell, contains approximately 1.35 to 5 percent phosphorus as an element on a dry weight bases (K-4). Compared to other macro-nutrients such as carbon, nitrogen, and silica, the typical occurrence in a cell of these elements relative to phosphorus as an atom basis is 106, 16, and 1 to 50 respectively (S-13). Because atom ratios of nutrients observed in natural receiving waters (e.g., lakes and oceans) are in some cases less those "typical" values seen in biological cells; it has been postulated that phosphorus is the nutrient limiting growth or productivity in these aquatic systems. It has been proposed further that by limiting the occurrence of phosphorus relative to the other nutrients, control of productivity in the aquatic system can be achieved (B-5).

"Eutrophication", translated from its Greek root means "to nourish well". In a modern sense it refers to the nutrient enrichment of waters, a natural occurring process. The enrichment of a lake results in its aging and eventual disappearance, an event occurring over a geologic time span. The limnologist defines this process in three stages. Initially an oligotrophic lake is characterized by a low concentration of nutrients, and oxygen rich waters supporting a small amount of productivity. Newly formed, the lake is usually deep. As the lake becomes a depository, sediments reduce its depth, nutrient enrichment increases productivity, and the resevoir of oxygen is being depleted by organic decay and mineralization. The lake has become eutrophic. At a condition midway between, the lake is said to be mesotrophic.

Imposed upon this process are the activities of man. His contribution of nutrients, and consequent acceleration of the increase in productivity is differentiated from the natural process, as "cultural eutrophication" (H-1). The devaluation of a recovery water as a natural resource is evidenced by the following symptoms:

(i) increased production of phytoplankton population with a shift of species from diatoms to greens, and the least desirable blue-green algae,

(ii) deterioration of water quality, particularly with respect to taste, clarity, and dissolved oxygen concentration,

(iii) increase in dissolved and suspended material particularly nutrients and organic matter,

(iv) decrease in the value of commercial fisheries caused by a change from game to coarse fish species,

(v) decrease in depth by an increase in sedimentation.

A clear and precise understanding of man's specific contributions to eutrophication or which of these should be regulated as either a cure or preventive measure has yet to be determined.

Of the twenty-one elements found in algae cells, Bartsch (B-5) reports that nine have been found to be growth limiting in certain lakes. Among the macro-nutrients, carbon (K-3, A-2, K-4), nitrogen (K-2), phosphorus (E-1, S-3), silica (S-3), and rarely sulphur have been so designated. Of the minor nutrients, manganese iron, cobalt and molybdenum (G-6) have been determined to be growth limiting. Thus a number of elements have assumed the role of limiting nutrients. Also as the ecosystem of a lake is a complex envirorment, a combination of nutrients may by their concentration limit productivity either simultaneously or in some sequence. Thus the concept of one nutrient being growth limiting universally is too simplistic. What is to be shown here is first that phosphorus has limited algae productivity in a number of lake ecosystems, and second the discharge of this element is more amendable to control than other nutrients.

The most dramatic example of a decrease in phosphorus input to a lake reducing phytoplankton productivity is the diversion of sewage from Lake Washington (E-1). Beginning in 1963, all sewage outfalls were rerouted from Lake Washington to the Puget Sound. This action meant a reduction in the nutrient budget of the lake of 50 percent for phosphorus and 15 percent for nitrogen. By 1971, improvement in the lake water quality was evidenced by:

(i) a decrease in phosphorus concentration to levels measured in 1950,

(ii) drop in chlorophyl concentration,

(iii) a decrease in dominance of blue-green algae species from 96 to 80 percent.

Interestingly, though the phosphorus concentration is continually decreasing, indicating the sediments are a sink for this element, neither nitrate nor carbon dioxide concentrations are. This suggests the major source of these latter nutrients is other than the sewage outfall.

Primary productivity in Lake Michigan (S-3) has shown to be limited by the levels of phosphorus and silica. The second nutrient deficiency is believed responsible for the shift of phytoplankton species from diatoms to greens, and blue-greens.

In the report to the International Joint Commission in 1969 (I-1), it was concluded that phosphorus is of importance in the enrichment of the lower Great Lakes. This conclusion is founded in part from the work of Vallentyne (V-1) for these waters. Vollenweider (V-2) has made a comparison of twenty different lakes located worldwide with respect to their phosphorus input and level of productivity. A correlation was found between the mass flux of phosphorus and lake depth and level of nutrient enrichment (i.e., oligo-, meso-, or eutrophic). Applying this correlation to the lower Great Lakes, the International Joint Commission concluded that Lake Ontario was in an mesotrophic state, and Lake Erie eutrophic. A reduction in the phosphorus flux, achieved by phosphate bans in detergents and treatment of sewage effluent for 95 percent phosphate removal, would return Lake Ontario to a oligotrophic state and the central and eastern basins of Lake Erie to a mesotrophic state (I-1). This prediction by the International Joint Commission was made on the bases of Vollenweider's correlation.

A second study of Lake Erie's central basin, "Project Hypo"in 1970 (B-24), assessed the rate of oxygen depletion and nutrient budgets in the hypolimnion. The conclusion from this investigation was that "phosphorus input to Lake Erie must be reduced immediately". If not, Burns et al. (B-24) believed productivity will continue to deplete oxygen until the bottom sediments subject to an anoxic enviroment become a phosphorus source, rather than sink.

Many authors in reporting phosphorus as a growth limiting nutrient have put forth maximum aqueous concentrations of phosphorus above which nuisance algae blooms will occur. Sawyer (S-1) from the study of seventeen Wisconsin lakes suggested that phosphorus concentrations should not exceed 10 ppb,nitrogen concentrations 300 ppb. Similarly Machenthun (M-1) and Chu (C-2) from their separate investigations set limits of 50 ppb. Kramer et al.(K-5) calculated from observations (V-2) of the minimum phosphorus concentrations needed to support cell growth, that 6 ppb should be considered as the excess concentration needed for a bloom.

All nutrients are recycled between the living and non-living phases of the ecosystems. This process is termed "biochemical cycling". The important difference in the cycles of nitrogen and carbon compared to phosphorus is the absence of a gaseous phase for the latter nutrient (L-7). The availability of nutrients from the atmosphere insures that the cycle is complete and continuous. For example, phytoplankton require carbon as its dioxide. This nutrient is available from either the aerobic decomposition of organic material (A-2) or the carbon dioxide-carbonate equilibria (M-17). Similarly, it has been shown that certain species of blue-green algae can fix nitrogen from the atmosphere when aquatic sources become deficient (H-4). Conversely, phosphorus like other rockbound nutrients such as calcium, potassium and manganese is recycled by the processes of erosion, sedimentation and biological activity. Deevey (D- 7) states that this "sedimentary cycle" is incomplete without an atmospheric resevoir. Also, he states that among the rockbound elements, "phosphorus is the scarcest in biological demand". Evidence of phosphorus being consolidated within the sediments has been observed. From "Project Hypo" (B-24), it was determined that 80 percent of the phosphorus was retained in the sediments under oxic conditions. In comparison only 56 percent of the nitrogen was retained. Similarily in Lake Washington (E-1), phosphorus concentrations were observed to decrease by a factor of four, once the influx had been reduced.

The source of a nutrient is an important factor in its control. From data reported to the International Joint Commission in 1969 (I-1) and 1973 (G-7), the following portions of the phosphorus influx to the lower Great Lakes were calculated to be contributed from point sources, (i.e., municipal and industrial effluents).

TABLE 20 PERCENTAGE OF PHOSPHORUS INFLUX FROM POINT SOURCE

Basin	1967	1972
Detroit-St Clair Rivers and Lake Erie	70%	53.5%
Niagara River and Lake Ontario	57%	49%

In the five year period, after action has been taken to remove phosphorus from wastewater and reduce phosphates in detergents, point sources are still significant. The point sources are much easier to collect and treat in comparison to distributed pollution sources arising from surface runoff and groundwaters (B-5).

I.2 PHOSPHORUS POLLUTION CONTROL CRITERIA

The focus of attention in North America with respect to the control of phosphorus pollution has been directed towards the Great Lakes. These five lakes are an invaluable natural resource; but the water quality of the lower two lakes is rapidly depreciating. In response the "Great Lakes Water Quality Agreement" (U-2) was signed by Canada and the United States in 1972. This international treaty calls for the total phosphorus effluent concentration not to exceed 1 mg/l from municipal sewage treatment plants whose capacity equals or exceeds 1 MGD. Industrial effluents are to be treated to an extent which is technologically practical. A schedule of the reduced total inflows of phosphorus to Lake Erie and Lake Ontario from 1972 to 1976 is specified in the treaty. It is worthwhile to note that the phosphorus loading to be achieved in 1976 of 0.56 and 0.47g./m /year for Lakes Erie and Ontario are above the influxes recommended by the International Joint Commission in 1969 (I-1) of 0.39 and 0.17g./m /year. Provincial and state governments in the Great Lakes basin have supplemented this international standard with local regulations, and in some cases a restriction or ban on the phosphates contained in detergents. These actions are summarized in Table 21.

TABLE 21

CRITERIA FOR PHOSPHORUS POLLUTION CONTROL

State or Province	Detergent	Effluent Criterion for total Phosphorus	Effective Deadline
Ontario	limit of 5% (P_2O_5)	<1 mg/1 or 80% removal	12-31-73 (L. Erie) 12-31-75 (L. Ontario)
Indiana	total ban*	<1 mg/1 (for discharge 20 lb P/day)	1-1 -73 (L. Michigan)
Michigan	limit to 8.7%	80% removal	12-1 -72 (L. Michigan 1-1 -74 (L. Superior) 11-1 -73 (L. Erie & Detroit R.)
New York	total ban	<1 mg/1 (for discharge >1 MGD)	1-1 -73 (L. Erie & L. Ontario)
Illinois	no action	<1 mg/1	1-1 -73 (L. Michigan) 1-1 -74 (Fox R.)
Ohio	no action**	<1 mg/1	12-1 -73 (All)
Pennyslvania	no action	<1 mg/1	1-1 -73 (L. Erie)
Wisconsin	no action	85% removal	3-1 -73 (L. Michigan & Fox R.) 12-31-74 (L. Superior)
Minnesota	no action	<1 mg/1	same as International Water Quality Agreement

* (does not include dishwashing and commercial detergents)

** (Akron, Ohio has a total ban)

The Congress of the United States has called for even more restrictive effluent standards in the Federal Water Pollution Control Act Amendments of 1972 (F-1). This law requires that the discharge of pollutants into navigatible waters be eliminated by 1985. A goal for 1983 is the achievement of a water quality sufficient for the protection of all wildlife fauna and for recreational use.

The Federal Enviromental Protection Agency has yet to define these objectives into specific effluent standards (M-6). The office, Chief of Engineers for the U.S. Army Corp has suggested effluent criteria to meet these "zero discharge of pollutant" goals. For phosphorus the Corp states that 0.02 mg/l is desirable, but that only 0.5 mg/l is a practical standard that can be consistently achieved with present treatment technology (U-1).

I.3 PHOSPHORUS CHARACTERISTICS IN WASTEWATER

In Ontario, the average total concentration of phosphorus in raw sewage was found to be 7.4 mg/l and to vary from 2.3 to 18 mg/l (B-20). Bargman et al. (B-2) observed from a weeklong survey that the influent phosphorus concentration reached a diurnal maximum and minimum and the amplitude of this cycle decreased from the beginning of the week toward the end. The type and distribution of phosphorus reported as typically characteristic of wastewaters are (G-9, D-1):

(i)	orthophosphate	40-45 percent
(ii)	polyphosphates	24-45 percent
(iii)	suspended phosphates	10-36 percent

There is a paucity of information (K-5) concerning the nature and concentration of organic phosphorus in wastewaters.

Orthophosphates are the result of erosion, the hydrolysis of polyphosphates, or the degradation of organic phosphorus. Polyphosphates are found primarily as two forms in wastewaters, pyro- and tripolyphosphate (H-2). These compounds are manmade and are the two most important constituents of phosphorus builders in detergent formulations. For example, sodium tripolyphosphate accounts for nearly 95 percent of the phosphates in laundry and powdered dishwashing detergents (G-10). Potassium pyrophosphate is used mainly in liquid detergents. An intermediate product formed in the hydrolysis of tripolyphosphate to the ortho-compound is pyrophosphate (H-2). Solid phosphates include both organic and inorganic forms. Organic compounds are believed to originate from food scraps and human waste. Inorganic forms are the result of the precipitation of metal salts, (e.g., calcium apatite (J-1)).

In the future, the phosphorus content of wastewater is anticipated to change in the following manner. The fraction of the total phosphorus concentration attributed to human wastes is expected to remain constant. The total mass loading from this source will increase due to increases in population, and as more households are connected to sewer systems. This latter factor has been particularily significant in the last decade. That fraction of phosphorus attributed to detergents can be expected to decrease. In the last decade, detergent phosphorus use per capita increased continually at an annual rate of 4.5 percent (B-24). This trend was a result of increased demand for detergents by the consumer and an increase in detergent phosphorus content from approximately 10.5 to 13 percent. This second factor has been reversed. For example, in Canada the phosphorus content in detergents is limited to 2.1 percent by weight, while in the states of New York, Indiana and Conneticut, a total ban is in effect. While the quantitative effect of this action is uncertain, the International Joint Commission in their 1973 report (G-7) stated that detergent reformulations may be impacting the phosphorus reductions to a greater extent than was contemplated.

I.4 METHODS OF PHOSPHORUS REMOVAL

Several separation processes that have widespread usage in the chemical industry have been specifically adapted for the removal of soluble and particulate phosphates from sewage. For example, three process functions that have successfully modified are:

(i) chemical precipitation,
(ii) adsorption,
(iii) ion exchange.

To this list, two biological treatment processes are added. One is modifications of the activated sludge process carried out to promote the "luxury uptake" of phosphates by the bacteria of a mixed culture. The other process is designed to promote phytoplankton activity in order to concentrate phosphorus in the algae cells, and then harvest these cells. Other treatment methods that are not designed exclusively for, but have beneficial removal of phosphates are:

(i) application of sewage to land,
(ii) electrodialysis,
(iii) distillation,
(iv) reverse osmosis.

All of these treatment methods are applied to point sources, (i.e., municipal and industrial wastewaters that have been collected by sewers).

Normally, conventional primary and/or secondary treatment of sewage is not adequate to meet phosphorus effluent standards. Typical removal efficiencies that have been reported are (B-5):

(i) primary treatment--10 percent,
(ii) conventional activated sludge process--40 percent,
(iii) trickling filter process--25 percent.

Though a number of processes have been demonstrated as effective for the removal of phosphates, only chemical precipitation has been given serious consideration in the Great Lakes basin. This process can be incorporated into conventional treatment plants with a minimum capital expenditure.

The following statistics indicate the extent to which the chemical precipitation method has been adopted. In Ontario by the end of 1973, 156 plants will be removing phosphates by chemical addition (G-7). These facilities service one third of the province's population. By the end of 1975, 57 additional treatment plants, serving the remaining population, will have this method on stream. In the United States, 252 plants are to be upgraded for phosphorus removal (G-7). Current progress, as of May 1973 (D-1), in implementing chemical precipitation techniques, is (for sewage treatment plants with a capacity equal or greater than 2 MGD):

(i) 40 plants are undergoing feasibility studies,
(ii) 32 plants are undergoing plant trials,
(iii) 34 facilities are under construction,
(iv) 63 facilities are operational.

The most common precipitating agents used to remove phosphates are calcium, aluminum and iron. These metals are usually added as the following salts:

(i) CaO or $Ca(OH)_2$ (commonly called unslaked and slaked lime,

(ii) $Al_2(SO_4)_3.14\ H_2O$ (commonly called alum),

(iii) $FeCl_3$, $FeCl_2$, $Fe_2(SO_4)_3$ and $FeSO_4$.

The process itself consists of three steps. First, the chemical precipitant is added to the wastewater as either a dry solid, slurry, or concentrated solution. Sufficient turbulence (mixing) is generated to obtain a uniform dispersion of the chemical. A precipitate is formed which is a mixture of insoluble hydroxides and phosphates when iron or aluminum is the agent, or these salts plus carbonates when calcium is used. Recht and Ghassemi (R-2) have shown that the aluminum or iron reaction is essentially instantaneous. In the case of calcium, however, Menar and Jenkins (J-2) reported the rate to be strongly dependent upon a number of variables, particulary solution pH, magnesium and carbonate concentrations.

The second step is particle growth usually termed flocculation. The precipitate is placed in a hydraulic regime of reduced shear or turbulence. The objective is to promote growth by increasing particle to particle collisions, but to maintain shear forces below a limit which would cause the breakup of newly formed floc particles. The last step is to remove these particles, usually by filtration or settling.

Initially, the approach had been to separate these process steps into three operations. The entire treatment scheme was then added after secondary treatment as a tertiary stage. An example is the facility at Lake Tahoe (S-9), where lime precipitation is used. More recently, the practice has been to add the chemical precipitant directly to primary or secondary treatment areas, and allow the removal process to operate simultaneously with bio-oxidation.

Operating experience gained from both laboratory and full scale plant experiments of the Biological-Chemical Treatment Method have been summarized. Rupke et al. (B-20, R-7) reported on the numerous jar studies and twenty-four plant trials carried out in Ontario. Minton and Carlson (M-9) reported on twenty-eight studies of combined treatment and sixteen of tertiary treatment completed in America and Europe. The pertinent observations and conclusions of these studies are discussed.

All authors agree that the prediction of the chemical dosage from the usual water quality parameters including the initial phosphorus concentration is largely uncertain and definitely not stoichiometric with respect to phosphorus. Lime requirements were found to be primarily dependent upon the initial alkalinity of the sewage. In the Ontario studies, ferric ion dosage showed a greater dependence upon the initial phosphorus level than aluminum. Both metals showed improved correlations in samples from secondary effluents, as compared to raw sewage. The uncertainty in specifying the chemical requirement needed to achieve a residual phosphorus concentration of 1 mg/l is shown in the range of chemical dosages found to be optimum at different locations. These are:

(i) lime --- (as $Ca(OH)_2$ 150-400 mg/l,
(ii) aluminum -- (as $Al_2(SO_4)_3 \cdot 14H_2O$) 100-300 mg/l,
(iii) ferric ion-- (as Fe^{3+}) 10-40 mg/l.

Rupke noted that the variability in performance of a precipitant increased with an increasing proportion of industrial wastewaters in the sewage.

These studies indicated that in plants with secondary treatment, the effluent channel from the aeration tank was the best location for chemical addition of aluminum and iron. Because of the solution pH necessary for precipitation to occur, lime is normally added only to raw sewage. Lime floc carried over from the primary clarifier was observed to resolve in the aeration tank as the pH decreased to a neutral value. This occurrence meant that a residual phosphorus concentration of 1 mg/l could not be obtained in the final effluent. For all chemicals, the intensity of mixing at the point of addition was found to be important. A uniform dispersion of the chemical is required to prevent localized changes in pH causing decreased removal efficiency. Both studies suggested the rate of chemical addition be coordinated to variations in the incoming flow. A feed forward control loop for chemical addition based on incoming phosphate concentration was considered infeasible; a feedback loop based on the effluent concentration was thought possible.

The addition of chemicals to a conventional biological treatment process was observed to yield both positive and negative benefits with respect to plant operation. Increased removal of suspended solids and materials exerting a biological oxygen demand was observed. In one study (B-10), in which lime was added to the primary clarifier of an activated sludge treatment plant, the reduction of biodegradable carbon in the primary area was sufficient to allow nitrification with 97 percent oxidation of ammonia, to occur in the activated sludge reactor. The Ontario studies demonstrated that overloading of the anaerobic digesters occurred from the increase in sludge production, particularly because of increased volatile solids. Also, these studies indicated no inhibitive effect of accumulated metal salts nor significant phosphorus resolution. in the digester. Minton, however, reported an elimination of the protozoan population in the aerobic reactors, but no significant decrease in the efficiency to remove carbonaceous material. All authors stated that the settlability of the combined chemical-biological floc was less than that of the biological floc alone. Therefore, it was recommended that the overflow rate of the final clarifiers not be allowed to exceed 650 to 700 gpd/ft^2. The dewatering properties of the sewage sludges were found to change with the addition of chemicals in the Ontario studies. The lime coagulent reduced the costs of conditioning chemicals (44 percent) and increased cake solids and filter yield (+39.4 percent). The presence of alum in secondary sludge caused little change. However, alum floc combined with primary sludges increased chemical conditioning costs (+20 percent) and decreased filter cake solids (-38.2 percent) and filter yield (-57.5 percent). As can be expected, the addition of coagulents increased the mass of suspended solids produced in every case. Depending upon the final concentration to which the chemical-biological sludge would settle, a corresponding increase in sludge volume also occurred. A summary of experience from the Ontario studies is given below.

TABLE 22 SUMMARY OF INCREASED SLUDGE PRODUCTION FROM CHEMICAL ADDITION

Source of Sludge	Mass of Dry Solids per MGD	Settled Solids Conc.	Wet Sludge Volume
	(as percent change)		
Aluminum and Ferric Salts			
Primary	+100%	-20%	150%
Secondary	+5-25%	-19%	+35%
Lime			
Primary	+200%	+100%	+50%
Secondary	+155%	+100%	+25%

The change in the dewatering properties of the combined sludge and their increased mass and volume can be expected to increase the final disposal costs of treatment plant sludges. This increment in cost has been calculated for the different types of sludge and chemical coagulants. The costs are calculated from the unit costs given by Bennett et al (B-7) for chemical conditioning, filtration, and incineration or haulage to a landfill of sewage sludges. The estimates apply for either incineration or a 30-40 mile haulage, as this is the break-even point for these operations.

TABLE 23 INCREMENT COST INCREASE FOR FINAL DISPOSAL OF COMBINED BIOLOGICAL-CHEMICAL SLUDGES

Chemical	Sludge	Incremental Cost /MGD treated
Aluminum and Ferric Salts	Primary	$37.2
Aluminum and Ferric Salts	Secondary	$47.7
Lime	Primary	$30.0
Lime	Secondary	$52.3

The "state of the art" is such that at each treatment plant, experiments are needed to determine which chemical is to be applied where, and at what concentration (M-8). Initially, all three precipitants are evaluated with grab samples using the jar test. From this, one chemical is selected and a dosage range established. Sampling at the treatment plant is continued over a three week period.

At least, ten samples taken at random is recommended (M-8). Again, the jar test is used to determine the residual total phosphorus concentration resulting from different chemical dosages (usually three). The procedure used in the jar test assesses the overall removal efficiency of the precipitation, particle growth, and settling steps.

As the characteristic of the sewage samples can be expected to vary over the three week period, a range of residual phosphate concentrations is obtained at each dosage. Each set of values is assumed to be representative of samplings from a population which is normally distributed. From each set, a probability curve is constructed which relates the frequency of occurrence of residual phosphorus concentrations at each chemical dosage. That dosage which provides a residual concentration of 1 mg/l, 80 percent of the time is selected for further plant trials. This approach of aggregating the data dampens variations in removal efficiency due to changing influent sewage characteristics, particularly the influent phosphorus concentration.

Chemical addition at the treatment plant is carried out for at least eight weeks. The purpose of these full scale trials is to:

(i) confirm the chemical dosage,

(ii) optimize the point of application,

(iii) provide information on the chemical-biological sludge characteristics,

(iv) provide preliminary cost data on operating expenses,

(v) confirm the suitability of existing facilities for phosphorus removal.

The cost of this type of research in determining chemical treatment procedures for over two hundred treatment facilities in Ontario will approach six million dollars (B-20). Unfortunately, the information from these studies is directly applicable to present treatment methods and wastewater characteristics. The utility of this data in the future is uncertain, when wastewater quality changes, as a result for example of new detergent formulations.

Other chemicals have been demonstrated to successfully precipitate phosphates. Sodium aluminate (B-3, B-4), though more expensive than alum, contains excess caustic which can be an advantage in maintaining pH, especially in wastewaters of low alkalinity. The use of "steel pickling liquor" has been demonstrated in municipal treatment plants in Detroit (D-10), Milwaukee (M-7), and Ontario (B-20). The liquor is a waste stream from the rolled steel finishing process and is an inexpensive source of the ferrous ion. Before phosphate precipitation can take place, this ion must be oxidized to the ferric ion, a reaction requiring more than two hours of aeration of sewage. Thus, its use is not feasible in a primary treatment plant. Recht and Ghassemi (R-3, R-4) demonstrated with secondary effluent samples that lanthanum, a rare earth, was a superior precipitant compared to either aluminum or iron. Lanthanum is more effective in four ways:

- (i) minimum residual phosphate concentrations occur over a wider pH range compared to aluminum or iron,
- (ii) polyphosphates are precipitated equally as well as orthophosphates,
- (iii) the chemical demand is approximately stoichiometric with respect to phosphorus,
- (iv) the extremely slight solubility of lanthanum phosphate results in residual phosphorus concentrations of less than .01 mg/l.

The cost of lanthanum requires that the precipitant be recovered and recycled for the process to be economically feasible. Chemical methods for the recovery of lanthanum have been demonstrated (R-5, W-1). Lanthanum chemistry with respect to precipitation and recovery is reviewed in greater detail in section 7.

Activated alumina appears to be the most promising adsorbent for the removal of phosphates (Y-1, A-3). The medium has been shown to be selective to ortho-, polyphosphate and arsenate ions, while the process causes no change in effluent pH, does not increase the dissolved solids concentration, and achieves efficient removal with residuals of less than .1 mg/l phosphorus reported. The adsorbent is regenerated with a strong base and the phosphates finally disposed of as a lime precipitate. Pilot plant trials have indicated its economic feasibility (A-4). Other adsorbents considered have used flotation as the separation process. For example, Grieves et al. (G-8) used a cationic surfactant only, Garrett et al. (G-3) used an aluminum hydroxide floc attached to foam, and Bhattacharyya et al. (B-8) used lanthanum and a surfactant aided foam.

Conventional ion exchange resins have been examined as possible removal media (A-5). Hummel (H-7) designed a process in which phosphorus was recovered as a fertilizer to offset operating costs. The common difficulty of ion exchange has been selectivity of the resin together with the concentration of competing anions (e.g., chlorides and sulphates) found in wastewater. Dougherty (D-11) developed the use of a ferric oxide gel which has partially overcome the selectivity problem.

As phosphorus is an essential cell nutrient, its removal from wastewater occurs through normal cell growth. Unfortunately ratios of carbon to phosphorus in sewage and in a normal heterotrophic bacteria cell are such that the latter ratio is greater. Thus only partial removal of phosphates are obtained (approaching 40 percent). However, Levin, and Shapiro (L-4) have reported that under certain conditions, the "luxury uptake" of phosphorus occurs with an increasing efficiency of removal. That is, the cells consume greater amounts of phosphorus than normally observed. Controversy exists as to whether this process is biological in nature as new evidence by Levin (L-5) and Carberry et al. (C-1) indicate, or is actually a chemical precipitation of phosphates with naturally occurring calcium as Menar and

Jenkin (M-5) propose. In any event, the conditions necessary for the "luxury uptake" of phosphorus by heterotrophic bacteria (activated sludge) are still ill-defined, and prevent this process having widespread applicability.

Azad and Borchardt (A-5) have demonstrated that autotrophic cells (algae) can take up an excess of phosphorus to a maximum of 10 percent dry weight as opposed to 1.6 percent measured for normal heterotrophic cultures (M-16). Thus, a symbiotic autotrophic-heterotrophic system offers potential. McKinney et al. (M-4) have proposed such an "activated-algae" system. The practical limitation is however that algae cells do not flocculate efficiently and thus their removal from the effluent is not yet economically feasible.

I.5 LANTHANUM: THE ELEMENT

Lanthanum is located in Group III-B of the periodic table with an atomic number of 57, and an atomic weight of 138.92. Its ground-state "outermost" electronic configuration "$5d^1 6s^2$" of the neutral atom indicates the existence of a transition series called the "rare earths or lanthanides". The elements of this series with atomic numbers 58 to 71 inclusive, are characterized by having additional electrons (necessary to yield elements of increasing atomic number) located in the inner, well shielded 4f orbitals. Fourteen electrons can be located in these orbitals and thus fourteen elements are known to exist. Though the 4f orbitals of the lanthanum atom are empty, the slight energy difference between 4f and 5d electrons and the resulting similarity of chemical properties results in lanthanum being classified as a rare earth for practical purposes (M-11).

Only two oxidation states are known for lanthanum, zero for the metal and plus three for the ion in aqueous solution. Tripositive lanthanide ions are significantly larger than other tripositive ions with the exception of the actinide elements. Of the "rare earths", lanthanum has the largest ion size because the electrons of successive elements are added to the 4f orbitals. The size and the highly ionic character of the lanthanum cation result in chemical properties desirable for a precipitant. The attraction of this cation to form complexes with anions is limited. Thus it can be expected that (M-9):

(i) the number of known complexes is limited,

(ii) the only anions associating will have a small size, large charge, or special chelating abilities,

(iii) the stabilities of such species with respect to dissociation into ion components will be less than for other tripositive metal ions.

This is best illustrated by the extent to which lanthanum hydrolizes in aqueous solution. Three complexes have been reported for lanthanum (B-9), at least five for aluminum (M-1) and four for the ferric ion (S-7). Similarly with respect to ion complexes with orthophosphate, one is reported for the lanthanum cation (R-1), eight for aluminum (S-7) and seven for iron (S-7). An increased tendency for a cation to form complexes, decreases its free ion concentration and thus increases the solubility of any of its salts.

The term "rare earth" as applied to lanthanum is a more appropriate adjective of its practical use, than its occurrence. The abundance of lanthanum in igneous rocks is 19 g./ton (T-4), making this element more available than lead (16 g./ton) or molybdenum (16 g./ton). Compared to the other lanthanides, it is fourth in magnitude of occurrence at 11.4 percent (R-8). Important mineral sources are:

(i)	monazite--a phosphate--	22% as La_2O_3	(W-3),
(ii)	bastnasite--a fluorocarbonate--	25.7% as La_2O_3	(W-3),
(iii)	euxenite--mixed salts--	2.9% as La_2O_3	(T-4).

These minerals are often sought primarily for other elements.

For example, monazite is the principle source of thorium (4-12% as ThO_2), an important nuclear fuel. Similarly euxenite is mined primarily for its tantalum and neobium content. Thus the "rare earth" elements are often byproducts, whose cost will in part be governed by the demand for these other elements (S-10).

The principle applications of lanthanum have been in the manufacture of special alloys, glass, and catalysts. In the metalurgical field, lanthanum is combined with indium to form a superconductor, with stainless steel to improve yield and workability, and with other "rare earths" to form "mischmetal", a di-graphitizing agent of cast iron (T-4). In glass, lanthanum imparts the qualities of low dispersion with a high refractive index (T-4). Lanthanum is also used to dope both hydrocarbon synthesizing and cracking catalysts (T-3).

Limited information is available on the toxicity of lanthanum to humans. For example, the effect of acute or chronic contact outside the body is unknown as well as chronic inhalation or ingestion (S-2). The intakes of acute amounts of this element is believed to result in readily reversible changes which disappear after exposure. The principle toxic affect of lanthanons is to delay blood clotting and thus cause hemorrhages. The mechanism of this effect is believed due to the trivalent charge of the cation changing the charge of the blood cell. In animal blood samples, lanthanum was found to cause reversal of charge of the red blood cells at concentrations of 0.3 molar (B-1). This concentration is at least two orders of magnitude greater than the initial lanthanum concentration to be used in sewage treatment.

TABLE 24

COMPOSITION OF MIXED RARE EARTH SALTS

(Product #52440 Molybdenum Corporate of America)*

Rare Earth Oxide Equivalent 46% minimum.**

Rare Earth	Content (Percent by weight of total Rare Earth present)
Lanthanum	60
Cerium	15
Neodymuim	17.5
Praseodymuim	7
all other Rare Earths	.5

* Current selling price 37¢/lb in 250 lb lots.

** Rare Earths in chloride form.

I.6 COMPARISON OF LANTHANUM, ALUMINUM AND IRON AS PHOSPHORUS PRECIPITANTS

The experimental studies of Recht et al. (R-2, R-3, R-4) allow comparison of the performance of lanthanum against the more commonly used precipitants, aluminum and iron under similar conditions. In Table 25, the minumum solubility and the pH range at which this minimum occurs is compared for the lanthanum, aluminum, ferric, and ferrous cations reacting with ortho-, pyro-, and tripolyphosphates separately. The ions are dissolved in distilled water. In every case, lanthanum outperforms by causing the lowest residual phosphorus concentration to occur over the widest pH range. This superior performance is also illustrated in Figures 21 to 24. Figure 21 shows as expected, that lanthanum orthophosphate is less soluble than the aluminum salt in a sample of secondary effluent.

Reaction rate experiments for the orthophosphate precipitation have been carried out for all four cations. Lanthanum, aluminum, and the ferric ion were found to react almost instantaneously, less than a second. Precipitation of the ferrous ion, however, was found to take from five minutes to two hours for completion, depending upon the initial solution pH and phosphorus concentration.

To estimate the molar ratio of cation to orthophospate necessary for complete removal, the percent phosphate removal was measured at different molar ratios. The solution pH was

was kept constant in the area of minimum solubility for each metal. Extrapolation of the curvilinear characteristic of removal efficiency versus the molar ratio indicated lanthanum to be the most efficient, 0.9 moles of lanthanum are required to remove one mole of orthophosphate, while 1.23 moles of the ferric ion, and 1.4 moles of aluminum are required.

The amount of water bound and unbound was measured for the orthophosphate precipitates. The lanthanum precipitate was found to contain less unbound water (i.e., water removed by drying in a dessicator at room temperature) at 0.73 percent by weight than the aluminum or ferric salts at 9.7 percent. This indicates the potential of better dewatering properties for the lanthanum salt. The quantity of bound water (i.e., moisture removed by drying at 104°C and ignition at 600°C) found in the lanthanum salt was also less, approximately 10 percent by weight compared to 17.5 percent for aluminum, and 18.5 percent for the ferric salt.

TABLE 25

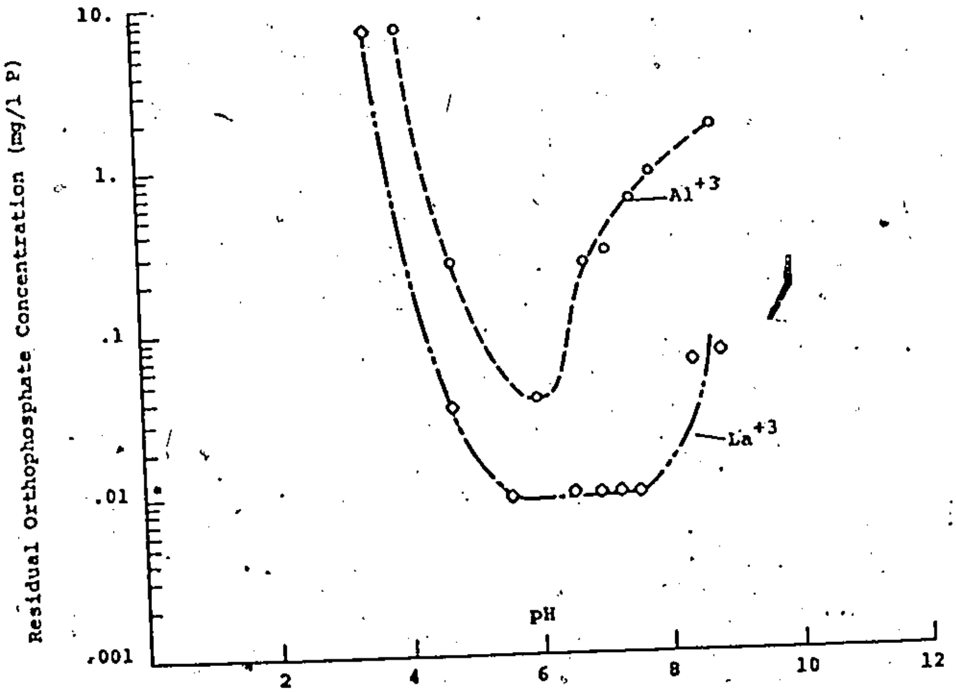
PHOSPHORUS PRECIPITATION

Cation	Lanthanum		Aluminum		Ferric Ion		Ferrous Ion
Orthophosphate - Distilled Water (initial concentration 12 mg/l P)							
Equivalence Ratio "Me: PO_4"	1:1	2:1	1:1	2:1	1:1	2:1	1:1
pH Range of Minimum Solubility	5-9	5-9	5-5.8	5.8-6.2	3.9-4.6	3.9-4.5	8
Phosphorus Residual at Minimum Solubility (mg/l)	<0.01*	<0.01*	2.6	.1	2.5	.07	.72**
Pyrophosphate - Distilled Water (initial concentration 18 mg/l P)							
Equivalence Ratio "Me: P_2O_7"	1:1	2:1	1:1	2:1	1:1	2:1	1:1
pH Range of Minimum Solubility	5.5-6.0	7-9		5.2-5.7	3.5-3.8	4.2-4.5	7.6-8
Phosphorus Residual at Minimum Solubility (mg/l)	0.06	.002		1.0	.4	.06	2.4
Tripolyphosphate - Distilled Water (initial concentration 21 mg/l P)							
Equivalence Ratio "Me: P_3O_{10}"	1:1	2:1	1:1	2:1	1:1	2:1	1:1
pH Range of Minimum Solubility	5.5-6.0	7-9		4.9-5.3		3.2-4.1	7.9
Phosphorus Residual at Minimum Solubility (mg/l)	0.06	0.002		4.0		.7	18.8

* represents a value below the detection limit

** precipitated as vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$

FIGURE 21. Precipitation of Orthophosphate from Wastewater Effluents at 2:1 cation-to-Orthophosphate Molar Ratio.



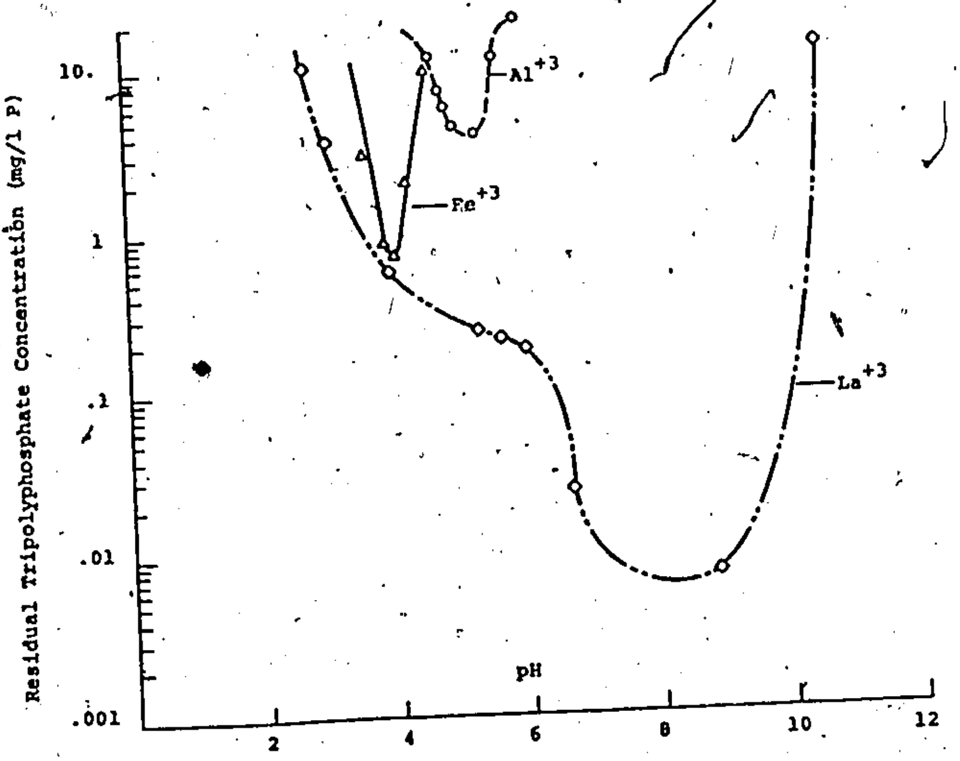
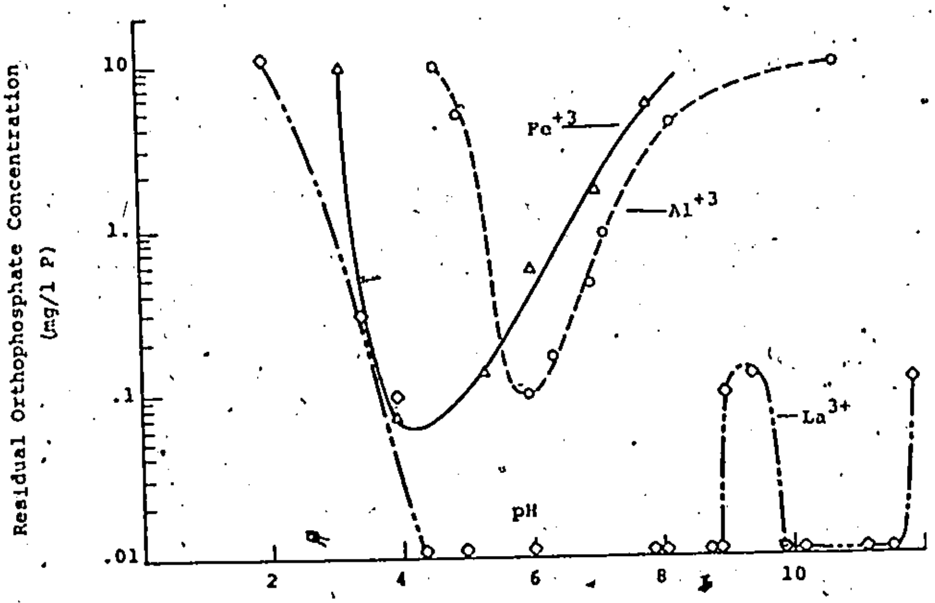


FIGURE 22. Precipitation of Tripolyphosphate at 2:1 cation-to- Tripolyphosphate Equivalence Ratio.

FIGURE 23. Precipitation of Orthophosphate at 2:1 Cation-to-Orthophosphate Equivalence Ratio.



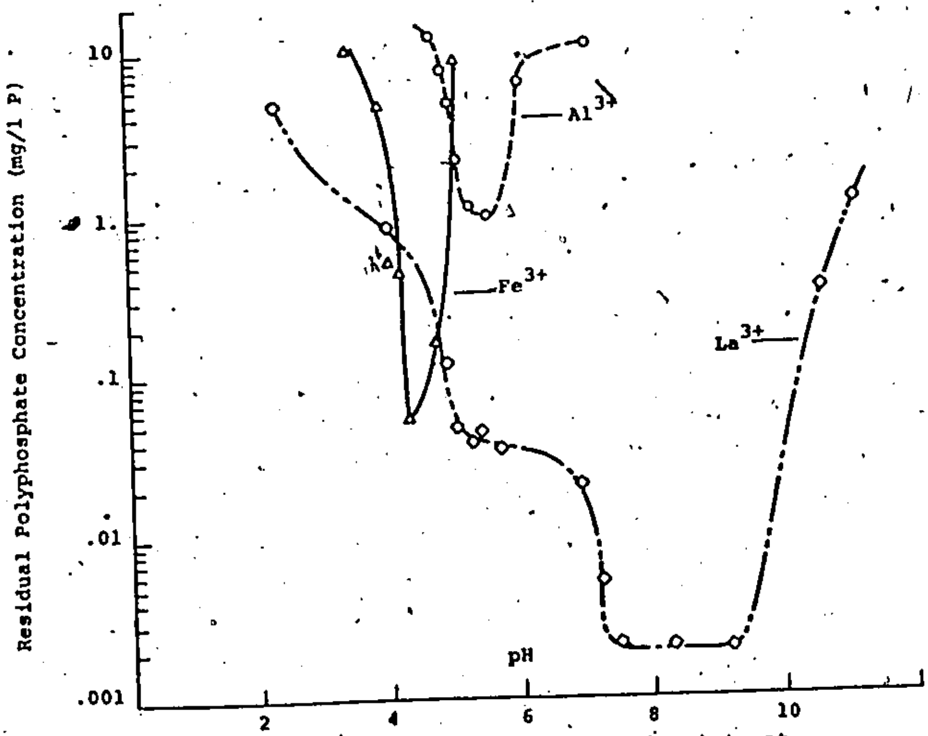


FIGURE 24. Precipitation of Pyrophosphate at 2:1 Cation-to-Pyrophosphate Equivalence Ratio.

Information reproduced from Recht et al. (R-2, R-3).

I.7 LANTHANUM RECOVERY SCHEMES

The cost of lanthanum salts requires that this metal be recovered if this precipitant is to be economically competitive with the more commonly used precipitants, aluminum and iron. Recht et al. (R-5) proposed the following scheme. The lanthanum phosphate precipitate is separated from the sewage effluent and then caused to react with a high strength caustic solution. Lanthanum is reprecipitated as a hydroxide from this solution, and then recycled back to the phosphorus removal process. The alkali is regenerated by precipitating the dissolved phosphates with lime, and then returned for further use with lanthanum phosphates. The process appears feasible, but little information was given as to the operating conditions necessary to achieve this regeneration.

Because of this lack of data, a preliminary investigation was carried out for this lanthanum recovery process (B-14). In addition, ion exchange methods were also evaluated as possible recovery processes (B-15). In this second approach, lanthanum phosphate is redissolved in an acid, and the metal concentrated by a cationic exchanger or the phosphates by an anionic resin. Both exchange methods proved infeasible. The rate of exchange of lanthanum with a commercial resin (Dowex 50-8x-25 mesh) was much slower in comparison to the exchange rate of other metals such as sodium, or calcium. The residence time needed for lanthanum exchange resulted in a reactor capacity that was not economically viable. The hydrogen ion concentration needed to dissolve the precipitant, resulted in the neutral trihydrogen orthophosphate complex being dominant species in the aqueous phase. Thus, only slight amounts of phosphate were concentrated on the anionic resin. Reaction rate studies of lanthanum phosphate in a strong caustic solution indicated that the rate of reaction and conversion to lanthanum hydroxide were encouraging, and thus this recovery scheme was investigated further.

M. Wasserlauf (W-1) measured the rate and extent of reaction for the conversion of lanthanum phosphate to the hydroxide in caustic solutions. The magnitude of these parameters as effected by the molar strength of the alkali ratios of alkali to phosphorus precipitate, temperature, and concentration of soluble phosphates in the alkali, was measured. All of these operating parameters were found to be significant. Similarly, two alkali regeneration schemes were also investigated. Lime precipitation and crystalization of sodium phosphates were considered as alternative schemes. From this study, the recovery scheme illustrated in Figure 25 is proposed. Wasserlauf estimated that the operating costs for chemicals and energy (evaporator) would be approximately 7¢ per 1000 gallons of wastewater and approximately 530 pounds of calcium hydroxyapatite would be produced for every million gallons of sewage treated for nutrient removal. From Table 23 the cost for disposal of additional biological-chemical sludges were found to range from 5.3¢/1000gal. for lime used in a secondary treatment plant to 3.7¢ for aluminum or iron used in a primary treatment process. Also the increment in sludge produced above normal operations was found to range from 2800 lb/MG to 1300 lb/MG for the same processes respectively (B-20). Thus, the lanthanum process is a feasible alternative in terms of the cost of sludge treatment and additional solids produced. Also, attention must be drawn as to the quality of sludge produced. The solids produced by the lanthanum recovery process, need not be buried in a landfill, but instead supplement the "phosphorus rock" used as a raw material in the production of condensed phosphates.

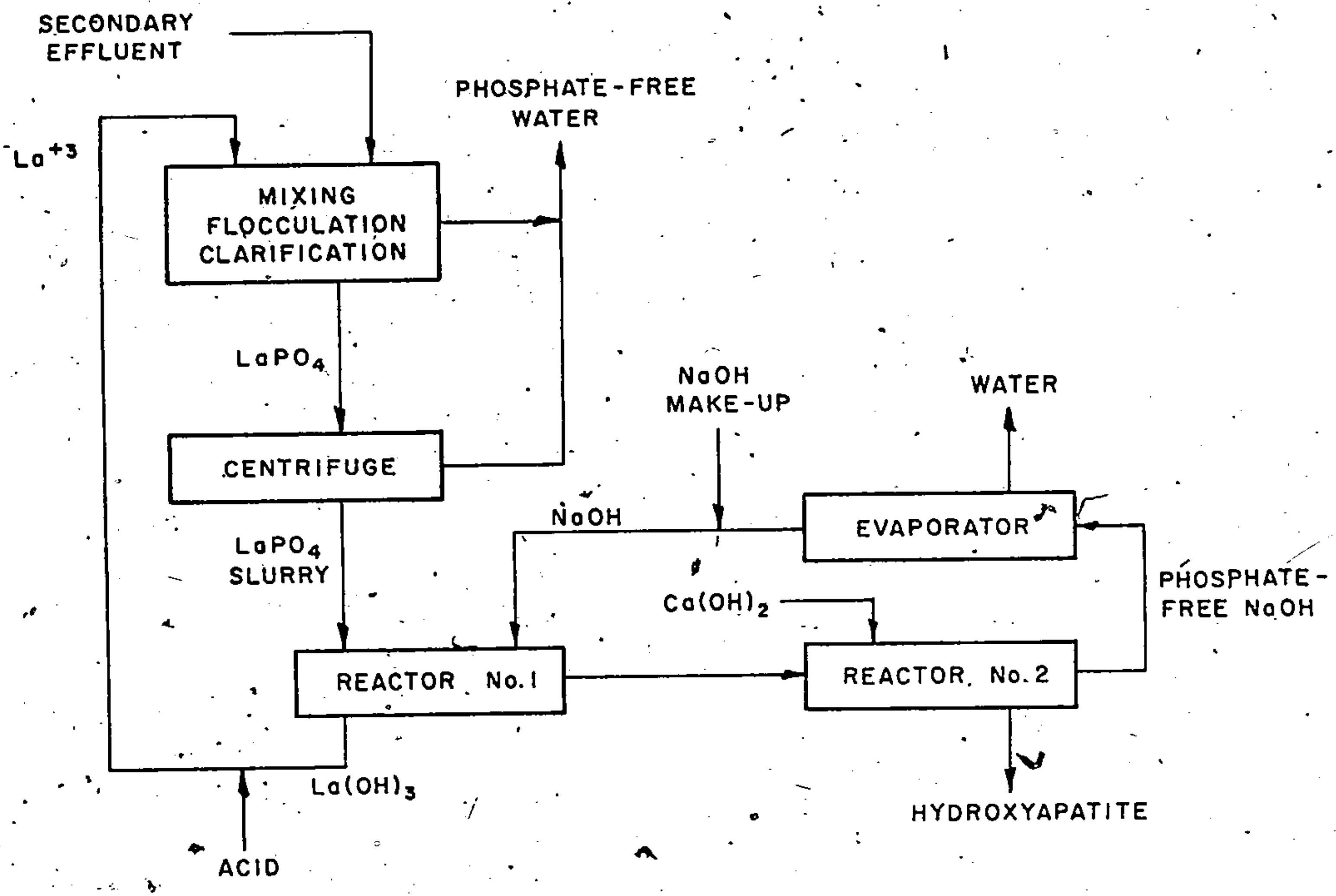


FIGURE 25 - LANTHANUM RECOVERY

I.8 APPLICATION OF EQUILIBRIUM MODELS TO NATURAL WATER SYSTEMS

Stumm and Morgan (S-14) have demonstrated extensively that equilibrium models based on the principles of classic chemical thermodynamics can be a useful tool in obtaining a theoritical description of natural water systems. This approach has been demonstrated by models of the chemical equilibrium in lakes (K-6), groundwater resevoirs (G-1), oceans (G-2, G-5, G-7) and wastewater treatment processes (L-3, M-14, F-2).

As Morgan (M-15) has previously stated, the idealized equilibrium model which has the essential features of the real system can be interpreted by a rigorous application of thermodynamics. Also when the model predictions do not agree with the real system, gaps in information or the limitations of considering the real system to be at equilibrium can be identified. The gaps in information may result from:

(i) pertinent chemical equilibria ignored in formulating reactions and species,

(ii) thermodynamic data that are incorrect or inadequate,

(iii) the data measured from the real system may not be consistent with those of the model (e.g., the model predicts a free ion concentration while only the total soluble, or soluble plus collodial concentrations of a substance can be measured),

(iv) temperature, pressure and activity coefficient-concentration corrections may need improvement.

Also, the real system may not be at a chemical equilibria because certain reactions may be so slow that a final state is not reached, and/or the influx of energy and material to the real system is of such a magnitude, that equilibrium cannot be approached. The chemical properties of a real system can be invariant with time (i.e., at steady state), but have values far removed from those at a true equilibrium.

Morgan (M-15) by the analysis of a system consisting of a reversible first order reaction has shown that the ratio of product and reactant approaches the equilibrium value, when the residence time of the system is much greater than the reaction rates. Often a large system such as a lake because of temperature and concentration gradients or because of the influx of material or energy to a specific area (e.g., epilimnion), cannot as a whole be considered at equilibrium. Components whose reactions are rapid can be at equilibrium in a local area with respect to their residence time there, (e.g., calcium, carbonates, and phosphates at sediment interface).

While not describing all of the past applications of chemical thermodynamics to describing natural water systems, a few illustrative examples are given. In attempting to define the composition of a natural water body such as a lake or ocean, the objective is to describe the present concentration in the aqueous phase resulting from the dissolution or erosion of sediments. Various minerals in the sediments are assumed to co-exist in equilibrium with water. These different solid phases represent an almost inexhaustable supply of components to the system. For example, only 7 percent of the sediments are believed to have reacted to account for the stabilization of sea water since its birth (S-8). In the interest of model simplicity, the problem is to select the significant solid phases which make the principle contributions to the aqueous solution. Also as these solid phases often represent well-structured crystal forms, they can be identified by X-ray diffraction techniques and thus suitable thermodynamic data are available for these minerals.

Confronted with this situation, Sillen (S-8) constructed a sea water model with seven solid phases, (quartz, kaolinite, illite, chlorite, montmorillonite, and philipaite) in equilibrium with eight aqueous components, H_2O-HCl-SiO_2-$Al(OH)_3$-NaOH-KOH-MgO. This left three independent variables to be specified, temperature, pressure and the chloride concentration. In a similar problem, Kramer (K-6) described the chemical composition of the Great Lakes in terms of seven solid phases, (calcite, dolomite, apatite, kaolinite, gibbsite, sodium and potassium feldspars), in equilibrium with the aqueous constituents (Ca^{2+}-Mg^{2+}-Na^+-K^+-H_2SiO_4-(SO_4^{2+}+Cl^-)-carbonate-H^+) and carbon dioxide. Temperature, pressure and the partial pressure of carbon dioxide were the independent variables.

The treatment of wastewater with a precipitant presents a different problem. Interest is centred on the solid phases produced, and the final composition of the aqueous solution. The solids produced are usually amorphous and thus not easily characterized by X-ray diffraction techniques and often have a higher solubility than corresponding well-structured forms. Therefore suitable thermodynamic data is not as plentiful. Also in the dissolution problem, as the solid phases are in excess, the stoichiometry is straightforward, while with precipitation the stoichiometry of components left in solution depends on how much and which solid phases are produced (F-2). This problem has influenced the choice of the computional technique chosen in this work.

Menar and Jenkins (J-1) used the solubility product concept to support their hypothesis, that the highly efficient phosphate removal observed at certain secondary treatment plants is the result of precipitation of phosphates with calcium occurring naturally in the wastewater. Leckie and Stumm (L-3) calculated the solubility of orthophosphate at equilibrium in the presence of calcium, aluminum and ferric ions to provide estimates of the lowest phosphate residuals that can be expected with a stoichiometric addition of chemicals. Their equilibrium models accounted for the acid dissociation and complex formation in the aqueous phase, and the formation of two solids phases. With the three different precipitants the following solid phases were assumed:

(i) variscite ($AlPO_4$) and gibbsite ($Al(OH)_3$),

(ii) strengite ($FePO_4$) and hydroxide ($Fe(OH)_3$),

(iii) calcium fluorapatite ($Ca_5(PO_4)_3F$) and calcite ($CaCO_3$),

(iv) calcium hydroxapatite ($Ca_5(PO_4)_3OH$) and calcite ($CaCO_3$),

(v) calcium phosphate ($CaHPO_4$) and calcite ($CaCO_3$),

(vi) calcium phosphate ($Ca_4H(PO_4)_3$ and calcite ($CaCO_3$).

Comparing the model predictions for the aluminum and ferric precipitants to the experimental data of Recht et al. (R-2), it is seen that the dependence of orthophosphate solubility upon pH agree, but that the residual phosphate concentrations predicted are approximately two orders of magnitude less than measured.

Leckie and Stumm state that an equilibrium model can be used to further understanding of the precipitation process as it occurrs in wastewater treatment. They propose that orthophosphates are precipitated from solution. Previous suggestions that simple counter-ion adsorption is the removal mechanism are rejected because of the high efficiency and the stoichiometry observed. Organic phosphorus compounds, being surface active, are however believed to be adsorbed onto the newly formed precipitates. Colloid suspensions of phosphorus material are destabilized by the metal ion, and then settle from solution. This last mechanism was shown by experiments with aluminum to account for the increment in chemical dosages added in order that phosphorus concentrations measured from settled samples agree with concentrations found in filtered samples.

The authors concluded treatment processes using aluminum and iron approximated an equilibrium state better than those using lime. The precipitation reactions of the first two metals were quick. Lime, however, formed a poorly structed solid which also reacted with water to form a surface complex. Also the reaction took place in two steps; first nuclei formation, then crystal growth over a longer period of time. The description of these rate processes is further complicated by the influence of particulate matter (particularly calcite) and the bicarbonate and hydrogen phosphate ions.

McCarty and Ferguson (F-2) developed an equilibrium model to describe the precipitation of orthophosphate with calcium from an aqueous environment like that found in an anaerobic sludge digester. The residence time of this treatment process approaches a month, thus a metastable condition can be expected. The model, consisting of six components ($Ca-Mg-PO_4-CO_3-H_2O-H^+$), considered the formation of seventeen soluble species and one of two pairs of solid phases. Calcium hydroxyapatite and calcite were assumed to occur at low magnesium concentration, while tricalcium phosphate and magnesium calcium carbonate at higher magnesium and carbonate levels. Predictions were made of the phosphate residual as affected by pH, initial carbonate, calcium, magnesium, and phosphate concentrations, and temperature. This information was compared to experimental data obtained from precipitation reactions occurring in artificial and actual digestor liquors. In addition to measuring soluble components, solid phases were partially characterized by X-ray diffraction, chemical analysis, and infrared spectra.

From the experimental work, it was concluded that magnesium had an important effect upon which solid phases were formed, and thus the residual phosphate concentration. Also, the aqueous component concentrations were used to estimate solubility parameters characteristic of a metastable equilibria occurring at 30°C after a period of 24 hours. These parameters replaced the solubility products of the four solid phases initially assumed in the equilibrium model. For each solid phase, its solubility parameter was observed to vary as to the initial concentrations of the components. Thus, for each precipitate, a set of solubility parameters was defined. The values of a set were defined at three pH regions (<8, 8-11, >11), three molar ratios of initial calcium to magnesium (1-2, <5, >5) and two molar ratios of calcium to carbonate (<.25, .25-1). With these revised parameters, predictions of the soluble components were within at least a factor of five of the values measured. The range of values assigned to each type of solid, and the uncertainty in model predictions suggest a more systematic approach is required in the design of experiments and use of this data to estimate parameters. At the least, such an approach would define if the variation in solubility parameters results from uncertainty in analytical measurements, or that one type of solid does have different solubilities at different initial conditions. Also, the error of the model predictions could be more precisely defined.

Morgan and Morel (M-14) in order to illustrate their computational method for determining chemical compositions at equilibria applied their program to an aqueous system of 788 soluble species, 83 possible solids, and one gas- phase. The thermodynamic data was taken from the literature. The system has some properties similar to sea water.

I.9 COMPUTATIONAL TECHNIQUES FOR THE COMPLEX CHEMICAL EQUILIBRIA PROBLEM

A number of generalized computer programs are available to solve the complex chemical equilibrium problem. In addition, computional techniques specialized for systems with particular sets of components and phases have been developed. For the problem here, three criteria were considered in selecting a calculation method. First, the input format must be structured so that soluble species and their corresponding reactions could be added or withdrawn easily. This requirement reflects the changing quality of wastewater, and different chemical species that can be expected therein, especially when municipal and industrial wastes are combined. Second, the solution algorithm must be able to select which solid phases have the best probability of occurrence at equilibrium from a set proposed. In modelling a precipitation process, it is not always possible to know, a-priori, which phases are present at equilibrium. Third, the program will be required to calculate the partial derivatives of the species's concentration with respect to both the equilibrium constant or free energy parameter, and the mass input of individual components to the system. These derivatives are required for formulating criteria on which to design experiments, estimating parameters, and calculating the magnitude of uncertainty associated with the model predictions.

The calculation of complex equilibria is a combination of thermodynamic fundamentals and numerical analysis. The fundamentals establish two sets of equations, a linear set of constraints (i.e., mass balances) which insure that the system obeys the laws of conservation of matter, and a nonlinear set which describe the distribution of species' concentrations in the system. If this distribution is described by the mass action laws and equilibrium constants (B-21, B-22), then a set of nonlinear algebraic equations is to be solved simultaneously, usually by an iterative technique. Alternatively, the Gibbs Free Energy contribution of each species to the system can be expressed by a logarithmic expression, the total energy is a weighted sum (D-2). The approach towards a solution, is the same as that for an optimization problem. The distribution at equilibrium is defined by those concentrations resulting in the minimum total free energy (S-4). Of course, the optimal solution is subject to the linear constraints of the mass balances.

Zelenznik and Gordon (Z-1) have carried out a comprehensive review (93 references) of the principles and equations describing chemical equilibria, the mathematical techniques applicable to this problem, and a critical survey of the equilibrium computation schemes that have been proposed. Since this survey, two general computer routines that ~~have~~ been published are "REDEQL" by Morel et al.(M-14 M-3) and "CHEMIST" by the Rand Corporation (C-5).

In "REDEQL", the solution method is based upon solving the nonlinear mass action equations subject to the mass balance constraints (i.e., the "equilibrium constant" approach). In "CHEMIST", the principle of free energy minimization is used to solve the problem. Both software packages are written to handle the general equilibrium problem. Information on species, component, and phase identification, reaction stoichiometry, equilibrium constants or free energy parameters, and the total quantity of each component in the system is handled by a series of matrices. Adding or deleting species from the chemical system is simply a matter of manipulating the appropriate matrix elements. Both programs require that a set of elements and/or molecular groups be stated from which any species in the chemical system can be created from a combination of these components. The notation scheme in "REDEQL" is, however, more restrictive. First all components are classed as metals or ligands with the exception of the hydrogen and hydroxide ions. Second, a species can be formed from only one ligand, one metal, and if needed the hydroxide or hydrogen ions. "CHEMIST" has no similar restriction on the combination of components. The "REDEQL" scheme does allow a more compact presentation of a large system, if not a completely general one.

By manipulation of the mass action relationships a minimum number of principal variables is found. It is only the concentration of these variables (usually the free metal and ligand concentrations) which must be solved, as all other species can be represented as functions of these. In the Rand program, each species concentration is treated as an unknown variable to be estimated directly.

In Morgan and Morel's program, if a solid phase has been specified, when at equilibrium it is actually completely dissolved, a negative concentration will be obtained. Similarily, if the presence of a particular solid equilibrium has not been forseen, the calculated set of concentrations will exceed the solubility product of the unspecified solid. Morgan and Morel have overcome this problem by incorporating in their solution path a check to determine if either a negative concentration has been calculated or a solubility product exceeded. If either case is so, the appropriate species is withdrawn or added to the system.

In the "CHEMIST" format if an uncertainty exists as to the possible importance of a solid phase, it is usually included. If the solubility of a species is such that under the input conditions it would not exist at equilibrium, the number of moles calculated to occur would be equal to the zero limit (i.e., 2×10^{-20} moles). For all practical purposes this can be considered equivalent to zero. The contribution of the species to the total free energy of the system and thus to the numerical solution is negligible. Care must be taken in that the total number of phases specified does not exceed the total number of components. This is a direct violation of the Gibbs' phase rule.

A subroutine package is available with "CHEMIST" to calculate many types of partial derivatives as described in Chapter II. This last factor plus the time when the Rand program became available resulted in "CHEMIST" being chosen for this study. The predictions from both computer programs of the same chemical system at equilibrium are compared in Chapter II.

I.10 DATA: EQUILIBRIUM REACTIONS

Collections of equilibrium constant data have been published. The most extensive record is "Stability Constants of Metal-Ion Complexes" compiled by Sillen and Martell (S-7). Particularly useful collections of thermodynamic data are given by Latimer (L-2) and Rossini et al. (R-6). Information concerning acid-dissociation, and metal ion complexes was obtained mainly from the literature. Information concerning the solubility of lanthanum salts and certain soluble complexes was determined by experiment. In the former case, the information was first obtained from the data collections and then when possible traced to its original source. This was done in order to evaluate the experimental conditions such as temperature, analytical methods, ionic strength of the medium, and the range of species concentrations. The procedure used to estimate the equilibrium constants was examined for assumptions concerning the presence of other complex species, and corrections made for ionic strength. For this work, constants estimated on a zero ionic strength bases were preferred. Table 26 summarizes the data with its source that was taken from the literature and used directly in the model. A review of previous work is given when experiments to measure lanthanum solubility and complexing parameters are described (Chapter IV).

TABLE 26

EQUILIBRIUM DATA (at 25°C)

Reaction	Equilibrium Constant $(-\log_{10})$	Free Energy Value*	Source
$HP_3O_{10}^{-4} \rightleftharpoons H^+ + P_3O_{10}^{-5}$	9.2	25.3	A
$H_2P_3O_{10}^{-3} \rightleftharpoons 2H^+ + P_3O_{10}^{-5}$	15.7	44.3	
$H_3P_3O_{10}^{-2} \rightleftharpoons 3H^+ + P_3O_{10}^{-5}$	18.0	53.6	
$NaP_3O_{10}^{-4} \rightleftharpoons Na^+ + P_3O_{10}^{-5}$	2.8	10.5	B
$KP_3O_{10}^{-4} \rightleftharpoons K^+ + P_3O_{10}^{-5}$	2.8	10.5	
$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$	12.325	32.394	C
$H_2PO_4^{-1} \rightleftharpoons 2H^+ + PO_4^{-3}$	19.532	53.001	D
$HCO_3^{-1} \rightleftharpoons H^+ + CO_3^{-2}$	10.329	27.798	E
$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{-2}$	16.681	46.438	F
$NaCO_3 \rightleftharpoons Na^+ + CO_3^{-2}$	1.27	-6.94	G
$NaHCO_3 \rightleftharpoons Na^+ + H^+ + CO_3^{-2}$	10.08	31.24	

*Free energy values have been divided by the constant RT and converted to the mole fraction scale.

TABLE 26 -(Cont'd)

Reaction	Equilibrium Constant (-log$_{10}$)	Free Energy Value	Source
$HP_2O_7^{-3} \rightleftharpoons H^+ + P_2O_7^{-4}$	9.4	25.7	A
$H_2P_2O_7^{-2} \rightleftharpoons 2H^+ + P_2O_7^{-4}$	16.1	45.1	
$H_3P_2O_7^{-1} \rightleftharpoons 3H^+ + P_2O_7^{-4}$	18.8	55.2	
$KP_2O_7^{-3} \rightleftharpoons K^+ + P_2O_7^{-4}$	2.3	9.3	B
$NaP_2O_7^{-3} \rightleftharpoons Na^+ + P_2O_7^{-4}$	2.3	9.3	
$CaH_2PO_4^+ \rightleftharpoons Ca^{2+} + 2H^+ + PO_4^-$	20.93	60.24	H
$CaHPO_4 \rightleftharpoons Ca^{2+} + H^+ + PO_4^-$	15.06	42.71	
$CaPO_4 \rightleftharpoons Ca^{2+} + PO_4^{-3}$	6.42	18.89	
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{-2}$	3.20	11.38	G
$CaHCO_3^+ \rightleftharpoons Ca^{2+} + H^+ + CO_3^{-2}$	11.59	34.71	
$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{-2}$	2.27	9.25	I
$CaOH^+ \rightleftharpoons Ca^{2+} + OH^-$	1.13	6.64	J
$CaP_3O_{10}^{-3} \rightleftharpoons Ca^{2+} + P_3O_{10}^{-5}$	8.1	22.7	B
$CaOHP_3O_{10}^{-4} \rightleftharpoons Ca^{2+} + P_3O_{10}^{-5} + OH^-$	10.4	32.0	

TABLE 26 -(Cont'd)

Reaction	Equilibrium Constant (-log$_{10}$)	Free Energy Value	Source
$CaP_2O_7^{-2} \rightleftharpoons Ca^{2+} + P_2O_7^{-4}$	6.8	19.7	B
$CaOHP_2O_7^{-3} \rightleftharpoons Ca^{2+} + P_2O_7^{-4} + OH^-$	8.9	28.5	
$MgHPO_4 \rightleftharpoons Mg^{2+} + H^+ + PO_4^{-3}$	15.23	43.10	K
$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{-2}$	3.40	11.84	G
$MgHCO_3 \rightleftharpoons Mg^{2+} + H^+ + CO_3^{-2}$	11.49	34.48	
$MgSO_4 \rightleftharpoons Mg^{2+} + SO_4^{-2}$	2.22	9.12	L
$MgP_3O_{10}^{-3} \rightleftharpoons Mg^{2+} + P_3O_{10}^{-5}$	8.6	23.8	B
$MgOHP_3O_{10}^{-4} \rightleftharpoons Mg^{2+} + P_3O_{10}^{-5} + OH^-$	11.0	33.4	
$MgP_2O_7^{-2} \rightleftharpoons Mg^{2+} + P_2O_7^{-4}$	7.2	20.6	B
$MgOHP_2O_7^{-3} \rightleftharpoons Mg^{2+} + OH^- + P_2O_7^{-4}$	9.3	29.4	
$MgOH^+ \rightleftharpoons Mg^{2+} + OH^-$	2.58	9.97	M
$LaSO_4 \rightleftharpoons La^{3+} = SO_4^-$	3.62	12.35	N

TABLE 26 -(Cont'd)

Reaction	Equilibrium Constant $(-\log_{10})$	Free Energy Value	Source
$H_2O \rightleftharpoons H^+ + OH^-$	13.997	40.257	O
<u>Solid Phases</u>			
$Ca_5(PO_4)_3OH \rightleftharpoons 5Ca^{2+} + 3PO_4^{-3} + OH^-$	48.	147.	P
$Mg_{.03}Ca_{.97}CO_3 \rightleftharpoons .97Ca^{2+} + .03Mg^{2+} = CO_3^{-2}$	6.6	25.8	
<u>Gaseous Phase</u>			
$CO_2{}^* \rightleftharpoons 2H^+ + CO_3^-$	21.6	61.9	Q & E

* Partial Pressure of CO_2 is set constant at 3×10^{-4} atmospheres.

(Equilibrium parameters are reported to the same number of significant figures as quoted by the respective authors.)

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APPENDIX II: "CHEMIST"-A CHEMICAL EQUILIBRIUM PROGRAM

II.1 INPUT INFORMATION FOR THE CHEMICAL EQUILIBRIUM PROBLEM

The algebraic terms used to describe the chemical system and the concept of storing information concerning these terms with the use of matrices is introduced in Chapter II. An aqueous calcium phosphate-carbonate system is used here as an example to illustrate:

- (i) the construction of these information matrices,
- (ii) the derivation of free energy parameters from equilibrium constants,
- (iii) the introduction of the data into the computer program itself.

The description of the chemical system is concisely presented in Figure 26. The 20 species assumed to exist at equilibrium are formed from linear combinations of 5 components. The sodium and chloride ions are inert components which do not enter into any of the reactions, but rather satisfy the charge balance in the system. The species are distributed among four phases or compartments, gaseous, liquid, and two solid phases. The components, species, and compartments are identified by alphanumeric parameters (with a limit of six letters) and numbers as shown in the row (components) and column (species) headings in Figure 26. The numbers are the values of the subscripts of the parameters "X_i" and "B_ℓ".

The stoichiometry for the formation reaction for each species are the elements $(a_{\ell i})$ in the column of that species.

Hence, each column represents a formula vector, and the set of these vectors the formula matrix. The case may arise that a species may coexist in more than one phase. This results in identical formula vectors. The double identification of a species by the name and compartment name or its number allows this situation to be accounted for. The presence of a species in two phases indicates a physical equilibrium (e.g., the occurrence of a species on both sides of a semipermeable membrane) with the free energy parameter being a distribution coefficient.

Gibbs (G-4) has shown that the components selected from a system containing many species for describing the composition of the system must be independent and sufficient in number to describe the composition completely. Brinkley (B-21) formulated the criterion that the rank of a matrix constructed from the formula vectors in the manner above equals the number of components needed to describe the system completely. Looking to the example in Figure 26 it is seen that the rank of formula matrix is seven, (i.e., the order of the largest minor whose determinant is nonsingular). Thus, the formula matrix presents a convenient format from which to determine if the condition stated by Gibbs is met. The choice of the independent components is usually not unique.

The column furthest to the right lists the mole quantities of each component in the chemical system. It is these values which are substituted on the right hand side of

FIGURE 26

MATRIX STORAGE OF EQUILIBRIUM DATA

ompartment No.	1	2																	3	4	
ubstance "X"	CO_2	Na^+	H^+	Ca^{2+}	Cl^-	OH^-	CO_3^{-2}	PO_4^{-3}	H_2CO_3	HCO_3^-	$H_2PO_4^-$	HPO_4	$CaCO_3$	$CaHCO_3^+$	$CaH_2PO_4^+$	$CaHPO_4$	$CaPO_4^-$	H_2O	$CaCO_3(s)$	Apatite	"B" Vector (moles)
pecies No. "i"	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
omponent No: "ℓ"																					
Components 1 Na^+		1																			.0055
2 H^+	2		1						2	1	2	1		1	2			1			55.341
3 Ca^{2+}				1									1	1	1		1		5	1	.002
4 Cl^-					1																.0040
5 OH^-						1												1	1		55.341
6 CO_3^{-2}	1						1		1	1			1	1						1	.002
7 PO_4^{-3}								1			1	1			1		1		3		0.0005
Free Energy Value "C_i"	-61.88	0	0	0	0	0	0	0	-46.44	-27.80	-52.98	-32.39	-11.38	-34.71	-60.24	-42.71	-18.89	-40.26	-146.64	25.76	

Compartments: 1-Atmosphere, 2-Aqueous, 3-Carbonate, 4-Apatite.

the mass balance equation (equation (7)) and define the size of the chemical system with respect to mass.

At the bottom of each column in Figure 26 , the value of the free energy parameter ("C_i") associated with that species is presented. These parameters are identified by the same subscript as the species. In Chapter II, it is stated that these values can be calculated directly from equilibrium constants. These constants are for the association reactions of the components which yield the species. An explanation of this statement is presented below.

The relationship between the equilibrium constant from the mass action equation and the change in Gibbs free energy at standard state for the formation reaction of species "i" is:

$$-\ln K_i = \Delta F_i^\circ/RT , \qquad \text{(II-1)}$$

where ΔF_i° represents the difference between the free energy at standard state of the product and reactants. This definition is represented by the following equation:

$$\Delta F_i^\circ/RT = (F_i^\circ - \sum_{i=1}^{M} a_{\ell i} F_\ell^\circ)/RT . \qquad \text{(II-2)}$$

The proof of this relationship is developed in most texts on thermodynamics, and one may be referred to either Denbigh (D-9) or Dantzig (D-3). Equating equations (II-1) and (II-2), it is seen that to evaluate the standard free energy constant for a product species from equilibrium constant data, the standard free energy constants of the components must be known. This problem is solved by setting the constants of the components to zero. Thus, the free energy constant of the product species is equal to an equilibrium constant describing that reaction.

The presence of a set of constraints allows this convention to be adopted. For a total of N species, if N equations are to be solved simultaneously, N equilibrium constants are required. For each algebraic constraint on the system (i.e., a conservation of mass equation), the number of equilibrium constants can be reduced by one. In the simultaneous system, an algebraic constraint on the mole numbers and an equilibrium constant are equivalent information (D-8). Thus, as the number of constraints is equal to the number of components, it is most convenient to set the free energy constants of the components to zero. Under this convention, the remaining free energy constants are determined relative to the arbitrary values that are set. The total free energy for the system will be different than if a finite free energy constant had been assigned to each component. Still the location of the minimum value of the free energy expression with respect to the chemical composition remains unchanged as illustrated by Danzig (D-3).

For the system modelled here, the pressure and temperature of the system are assumed to remain constant at 1 atm. and 25 or 5°C respectively. The effect of these variables is taken into account by the values selected for the equilibrium constants.

As shown in Figure 26, the equilibrium constants of species in the aqueous phase are for association reactions in which ion complexes are formed. These constants are often reported on the molal (moles per kilogram of solvent), or molar (moles per litre solution) scale. The equilibrium constant will have units equal to the concentration scale raised to the exponent Δn, where Δn ~~is~~ equal to the difference between the stoichiometric coefficients of product less reactants. Conversion to the mole fraction scale is simply made by multiplying the number of moles of solvent per unit mass or volume raised to the exponent $-\Delta n$ with the equilibrium constant (D-8).

Again looking to Figure 26, it is seen that each precipitate is assumed to exist alone in a separate phase or compartment. This convention was adopted in all of the systems modelled here. This convention is in keeping with the definition of the solubility product in which the activity and hence mole fraction of the solid phase is assumed to be unity (S-14). The solubility constant is equal to the reciprocal of the equilibrium constant for the formation reaction of the solid phase. The conversion of the concentration units of the aqueous components is the same as above except that the exponent is raised to the sum of the stoichiometric coefficients of the components. Assigning more than one solid species to a compartment is equivalent to assuming the formation of a homogeneous solid solution. For a discussion of the occurrence of this special situation, the reader is referred to Stumm and Morgan (S-14).

Just as in this example, carbon dioxide is the only gaseous species assumed to be in equilibrium with the aqueous phase in the systems modelled here. It is also assumed that the carbon dioxide concentration is constant at $3x10^{-4}$ atm. This concentration level is defined by the value of equilibrium constant and hence the free energy value. The level is kept constant because carbon dioxide is the only species in the gas compartment and therefore its mole fraction is unity. This assumption implies that the finite volume of the aqueous solution is insufficient to affect the composition of the atmosphere at its interface.

Data for the chemical equilibrium problem is introduced by a set of subroutines in the Rand software package. A number of methods are available to introduce this information and are described in the Rand Computer Manuals (D-8, C-5). Only the method used in this work will be reviewed briefly.

The operation is begun by a call to the subroutine "START" from the main program. "START" zeroes out the common storage and sets many of the computer parameters to nominal values (e.g., iteration limits, minimum mole numbers of species, etc.). This subprogram is called at the beginning of each new problem. A call to the subroutine "INPUT" immediately follows. The majority of data needed is illustrated by the example in Figure 26. "INPUT" processes portions of information itself and calls other subroutines internally to receive the remainder. After a call to "INPUT" the following data package must be available to the main program.

First, a card with a title in columns 2 to 72 is needed. This title is printed out at the time it is read and at each new page of printing. Subsequent title cards may follow with information between columns 7 to 72 but are printed out only when read.

Second, an optional series of cards may follow which revise the values of the computer parameters set by "START". Each type of parameter is changed by a card identifying the parameter's name, (starting at column 1), followed by a second card with the parameter value. Parameter names, parameter values, nominally set by "START" and their input format is summarized in Table 27. These computer parameters assume the following roles:

(i) "LIMIT"-sets the maximum number of iterations for the numerical solution techniques,

(ii) "LITER"-sets the number of moles of solvent per litre,

(iii) "RT"-equals the product of the gas constant and absolute ambient temperature,

(iv) "TOL1"-error criterion which determines when method II is substituted for method I in the numerical solution technique,

(v) "TOL2"-error criterion which defines when a solution is reached,

(vi) "XMIN"-minimum mole number for a species,

(vii) "XSTART"-initial guess for mole number of each species if no other value is supplied,

(viii) "BARMIN"-minimum sum of moles per compartment,

(ix) "SLACKS"-represents a dummy species that prevents a compartment from disappearing.

The total number of moles for each component is calculated as the sum of five groups, with each group multiplied by a factor. This arrangement allows the magnitude of certain components to be changed easily, while the others remain constant. These five group factors are first identified by a card with "MULTIPLIERS" written in the first eleven columns; followed by a card containing these factors in five floating point fields with a dimension of twelve. Without these cards, the first factor has a nominal value of one, the others zero.

The operation to read in component data begins with the control card "ROWS", (written in columns 1-4). This card directs the subprogram "INPUT" to call the subprogram "ROWS". On the following cards, the component name is written as an alphanumeric word in the first twelve columns. The contribution of each group as a floating point or exponential number in the next five twelve column sets. The component number is decided by the order in which they appear. This operation is concluded by the control card "END" (columns 1-3). The sum of the products of each group and its factor is calculated automatically.

The remaining equilibrium data on species is read by the subroutine "MATRIX", called by a control card (subroutine name in columns 1-6). The second card contains the compartment name (columns 1-12). Third and succeeding cards contain species information for that compartment listed as:

(i) species name (alphanumeric element)-columns 1-12,

(ii) free energy parameter (floating point number)-columns 13-24,

(iii) stoichiometric coefficient (floating point number) columns 25-30,

(iv) first six letters of the component name (alphanumeric element)-columns 31-36.

Additional stoichiometric coefficients, and component names are listed in succeeding twelve column sets to column 72, and then on following cards beginning in column 25 if needed. The procedure is repeated for each compartment and terminated by an "END" control card. Again, compartment and species numbers are determined by the order in which they are read in.

Initial estimates of the species' mole numbers are read in by the subroutine "VECTORX" (columns 1-7). Estimates are placed on following cards with the compartment name in columns 1-12, and estimates (floating point or exponential number) listed in order of the species' numbers in twelve column sets to column 66. The compartment name appears on each card with the estimates. This operation is optional. Control is returned back to the main program by the control card "RETURN" (columns 1-6).

The use of these control cards with data taken from the example problem in this section is illustrated in Table 28.

TABLE 27

COMPUTER PARAMETER DATA CARDS

Parameter-First Card Name	Nominal-Second Card Value	Input Format
LIMIT	40	Integer field - 4 columns
LITER	55.393333	Floating point field - 12 columns
RT	592.16	Floating point field - 12 columns
TOLERANCES (for the parameters)		
TOL1	10^{-2}	Floating point fields - 12 columns each
TOL2	10^{-5}	
XMIN	10^{-24}	
XSTART	10^{-6}	
BARMIN	10^{-20}	
SLACKS	2×10^{-20}	

TABLE 28

EXAMPLE OF INPUT DATA FOR FIGURE 26

PRECIPITATION OF CALCIUM PHOSPHATE AND CARBONATE

FREE ENERGY CONSTANTS EVALUATED AT 25 DEGREES CENTIGRADE

```
LITER
 55.340789
MULTIPLIERS
 1.000
ROWS
NA+           0.0055
H+            55.341
CA+2          0.002
CL-           0.0040
OH-           55.341
CO3-2         0.002
PO4-3         .0005
END
MATRIX
ATMOSPHERE
       CO2    -61.88     1.     CO3-2   2.    H+
LIQUID
       NA+               1.0    NA+
       H+                1.0    H+
       CA+2              1.0    CA+2
       CL-               1.     CL-
       OH-               1.0    OH-
       CO3-2             1.0    CO3-2
       PO4-3             1.0    PO4-3
       H2CO3  -46.44     2.0    H+     1.0    CO3-2
       HCO3-  -27.80     1.0    H+     1.0    CO3-2
```

```
      H2PO4  -52.98      2.0    H+     1.0    PO4-3
      HPO4   -32.39      1.0    H+     1.0    PO4-3
      CACO3  -11.38      1.     CA+2   1.     CO3-2
      CAHCO3-34.71       1.     CA+2   1.     H+      1.    CO3-2
      CAH2P  -60.24      1.     CA+2   2.     H+      1.    PO4-3
      CAHP   -42.71      1.     CA+2   1.     H+      1.    PO4-3
      CAP    -18.89      1.     CA+2   1.     PO4-3
      H2O    -40.26      1.0    H+     1.0    OH-
CARBONATE
      CACO3*-25.76       1.     CA+2   1.     CO3-2
APATITE
      HAP    -146.64     5.     CA+2   3.     PO4-3  1.    OH-
END
RETURN
```

II.2 PROJECTION METHOD

The prior estimate of the mole numbers "X_i" is designated as "Y_i". When substituted into the mass balance equation, this prior estimate generates an error term "G_ℓ" for each component. This error is given by the expression:

$$G_\ell = B_\ell - \sum_{i=1}^{N} a_{\ell i} Y_i . \qquad \text{(II-3)}$$

for $\ell=1,2,\ldots M$

The difference between the true value of the mole numbers and the prior estimate is given by the following expression:

$$X_i = Y_i + \theta_i . \qquad \text{(II-4)}$$

for $i=1,2,\ldots N$

Substituting the above expression into the mass balance equations and by rearrangement and combination of equation (II-3), the following relationship is found to relate the deviations from the mole numbers and the errors produced in the mass balance equation:

$$G_\ell = \sum_{i=1}^{N} a_{\ell i} \theta_i . \qquad \text{(II-5)}$$

for $\ell=1,2,\ldots M$

To obtain a positive feasible solution, the problem remains to choose θ_i such that the sum of Y_i and θ_i are greater than zero for all possible values of i. This cannot be done with complete certainty, but we can choose values of θ_i which are small. This is done by choosing values of θ_i which minimize the expression:

$$\sum_{i=1}^{N} W_i \theta_i^2$$

(II-6)

and still satisfy the mass balance constraints. The term "W_i" in this expression is a weighting factor. The above problem is solved by using Lagrange multipliers. The optimization problem with the mass balance constraints is expressed as :

$$L = \frac{1}{2}\sum_{i=1}^{N} W_i \theta_i^2 - \Sigma_{\ell=1}^{M} \pi_\ell \Big(\sum_{i=1}^{N} a_{\ell i}\, \theta_i - G_\ell\Big).$$

(II-7)

where π_ℓ are Lagrange multipliers. If a partial differentiation of this expression with respect to θ_i is performed and the result set to zero, the following expression results :

for i=1,2,....N $$W_i\, \theta_i = \sum_{\ell=1}^{M} a_{\ell i}\, \pi_\ell .$$ (II-8)

The correction factor "θ_i" is eliminated by the substitution of equation (II-8) into equation (II-5). The following expression is obtained :

$$G_j = \sum_{\ell=1}^{M} \Big\{\pi_\ell \Big(\sum_{i=1}^{N} \frac{a_{\ell i}\, a_{ji}}{W_i}\Big)\Big\} .$$ (II-9)

for j=1,2,....M

Experience has shown that a reciprocal of the prior estimate is a good choice for the weighting factor (i.e. W_i is equal to $1/Y_i$). The product of the stoichiometric coefficients and weighting factor can be represented by one term as shown by the following:

$$q_{\ell j} = \sum_{i=1}^{N} a_{\ell i}\, a_{ji}\, Y_i \quad \text{(II-10)}$$

for j=1,2,....M

ℓ=1,2,....M

Substitution of this new constant into equation (II-9), we have a set of linear equations which may be solved simultaneously for the Lagrange multipliers π_ℓ.

$$G_j = \sum_{\ell=1}^{M} q_{\ell j}\, \pi_\ell \quad \text{(II-11)}$$

for j=1,2,....M

The set of correction factors, "Θ_i", can be obtained by substitution of the values obtained from the multipliers into equation (II-8). Finally, from the correction factors a new set of estimates for mole numbers is obtained from equation (II-4). If any element of this new set is zero or negative, the projection method has failed. Should this happen, the linear programming method is then called to obtain the solution. The projection method is programmed within the subroutine "SOLVE" and initiated from here.

II.3 LINEAR PROGRAMMING METHOD

Linear programming problem is defined by a set of linear constraints as represented by the mass balance equations and objective function. This function is defined as an accumulative product of the mole numbers "X_i" and cost constants "k_i" as shown:

$$L = \sum_{i=1}^{N} X_i \, k_i \, . \qquad \text{(II-12)}$$

A solution to the linear programming problem is defined as that set of mole numbers which are feasible with respect to the mass balance equation and yield a minimum value with respect to the objective function. Though more than one solution may exist, interest is upon finding a solution. The mechanics of solving a linear programming problem are thoroughly reviewed in Dantzig (D-4). A solution to the linear programming problem is found by solving two problems. With the first, the objective is to find a positive feasible solution. This problem is stated in the following manner. The mole numbers are defined in terms of a set of elements and a constant:

$$X_i = Y_i + Y_{N+1} \, . \qquad \text{(II-13)}$$

for i=1,2,....N

A feasible solution is defined, if Y_{N+1} is positive and all elements of Y_I are nonnegative. To guarantee that Y_{N+1} is positive, we can attempt to maximize its value. This is done by setting all other cost constants to zero and k_{N+1} to -1. Minimizing the objective function "L" maximizes Y_{N+1}. The mass balance constraints are rewritten as:

$$\sum_{i=1}^{N} a_{\ell i} Y_i + \sum_{i=1}^{N} (a_{\ell i}) Y_{N+1} = B_\ell \qquad \text{(II-14)}$$

for $\ell=1,2,\ldots,N$

The problem is then solved for N+1 unknowns. If the solution to this problem results in Y_{N+1} being greater than zero, then by equation (II-13) we have a positive, feasible solution. Should Y_{N+1} be equal to zero, then the chemical equilibrium problem is said to be degenerate, as there is strictly no positive solution to the problem. This degeneracy usually arises from a mistake in defining the species and components of the system.

The object of the second problem is to find a set of mole numbers which approach those of the optimum solution. First the cost constants are equated to the free energy constants, C_i, while the last constant (i.e., C_{N+1}) is set to zero. This is equivalent to linearizing the free energy equation (5) by assuming that the logarithmic concentration term is negligible. An additional constraint is added to the mass balance set in the form of:

$$Y_{N+1} = B_{M+1} \qquad \text{(II-15)}$$

where the extra component B_{M+1} is ~~some~~ multiple between zero and 1 of Y_{N+1}. The problem is then solved.

This solution is improved by iterative steps. The number of iterations attempted is equal to the number of compartments or phases defined in this system. After each trial, the cost constants are equated to the following approximation of the free energy function:

$$k_i = C_i + \hat{X}_i - 1. \qquad \text{(II-16)}$$

for i=1,2,....N

Now, the logarithmic term has no longer been ignored, but is approximated by the linear term. The new estimate for the mole number for the next trial is calculated as the average of the present estimate and the previous estimates weighted as to the number of iterations.

The computation for the linear programming problems is handled by two subroutines. The subroutine "LP" arranges the input data into a suitable format. For example, the extra constraints are created and the cost constants set to their appropriate values. The subroutine "SIMPLE" is used to solve the general linear programming problem of minimizing equation (II-12) and subject to the constraints as represented by equation (II-14). The final set of mole numbers X_i are then calculated from the N+1 values of Y_i as defined by equation (II-15). This set then forms the initial estimate for the next program step.

II.4 THE LINEAR LOGARITHMIC PROBLEM

The search technique and computer logarithm were developed for what is called the general "Linear Logarithmic" programming problem (D-4). This problem is defined as minimizing the function of ϕ where it is given by:

$$\phi = \sum_{i=1}^{N} x_i \, (c_i + d_i \ln x_i) \qquad \text{(II-17)}$$

and subject to the constraints given by:

$$\text{for } \ell = 1,2,\ldots.M \qquad \sum_{i=1}^{N} a_{\ell i} \, x_i = b_\ell . \qquad \text{(II-18)}$$

The free energy expression, equation (8), differs from this form in the logarithmic term. The latter expression is manipulated into the general form in the following manner.

If the mole fraction, $\hat{X}_i$. is expanded into its component parts, then the free energy expression becomes:

$$F_{\text{system}} = \sum_{i=1}^{N} X_i \, (C_i + \ln X_i) - \sum_{i=1}^{N} X_i \ln \bar{X}_k{}' \qquad \text{(II-19)}$$

where the subscript "k" is determined by the subscript "i" as to which set it pertains. The first summation had the form of the general problem; the second summation is converted by:

(i) creating "P" new species, each of which is equivalent to the sum of the mole numbers, "X_k" for the Pth compartment. The total number of species is now $N_t = N + P$.

(ii) setting free energy constants to zero and the constant "d_i" to -1 for these constants associated with the new species.

After using those elements defined as zero, the free energy expression in its general form is:

$$F_{system} = \sum_{i=1}^{N} X_i \, (C_i + \ell n \, X_i) - \sum_{i=N+1}^{N_t} X_i \, \ell n \, X_i \qquad \text{(II-20)}$$

where for $i > N$, $X_i = \bar{X}_k$.

Since these new species enter into no reactions, P new components must be created and added to the set of mass balance constraints. The total number of constraints is now $M_t = M + P$. These extra constraints assume the general form by the following choice of parameters:

(i) for $\ell > M$, $B_\ell = 0$,

(ii) for $\ell > M$ and $i \leq N$ and in the compartment $P = \ell - M$, $a_{\ell i} = 1$,

(iii) for $\ell > M$ and $i \leq N$ and are not in the compartment $P = \ell - M$, $a_{\ell i} = 0$,

(iv) for $\ell > M$ and $\ell - M \neq i - N$, $a_{\ell i} = 0$,

(v) for $\ell \leq M$ and $i > N$, $a_{\ell i} = 0$.

Substituting these coefficients, the constraint equation reduces to a definition that X_i, for i is greater than N, is equivalent to the sum of the mole numbers for the compartment, $P = \ell - M$. This conversion of the free energy expression to the general form is reviewed by Clasen (C-3).

The constraints imposed upon the optimization problem are handled by the use of the Lagrange multipliers.

As a single expression, the "Linear Logarithmic" problem is given by:

$$L = \sum_{i=1}^{N_t} X_i \,(C_i + d_i \,\ln X_i) - \sum_{\ell=1}^{M_t} \pi_\ell \Big(\sum_{i=1}^{N_t} a_{\ell i}\, X_i - B_\ell\Big). \tag{II-21}$$

In theory, a set of values of "X_i" and "π_ℓ" which minimize "L" can be found by solving the $M_t + N_t$ equations simultaneously in terms of these elements. M_t of these equations are represented by the constraints as shown by equation (II-18). N_t of these equations are derived by equating the partial derivatives of equation (II-21) with respect to "X_i" to zero. This operation resulted in the following expression:

$$\ln X_i = d_i^{-1} \Big\{\sum_{\ell=1}^{M_t} \pi_\ell \, a_{\ell i} - C_i - d_i\Big\}. \tag{II-22}$$

for $i=1,2,\ldots N_t$

As this expression is nonlinear, the two sets of equations can not be solved directly. An iterate technique is required. Use of the estimates for "X_i" obtained from the Projection or Linear Programming technique are used to linearize the expression for "X_i". It is assumed that these estimates termed "Y_i" are sufficiently close to the true estimate to enable "X_i" to be represented by the first order terms of a Taylor series. That is:

$$\ln X_i = \ln Y_i + \frac{X_i - Y_i}{Y_i} + \text{higher order terms.} \tag{II-23}$$

for $i=1,2,\ldots N_t$

Upon substitution of this approximation, the expression for "X_i" becomes:

$$X_i = Y_i \{d_i^{-1} \sum_{\ell=1}^{M_t} \pi_\ell a_{\ell i} - d_i^{-1} C_i - \ln Y_i\}.$$

for $i=1,2,\ldots N_t$ (II-24)

The right hand side of this expression is substituted for the variable "X_i" in the constraint equation. Upon substitution, rearrangement, and summation, a set of M_t linear equations results for the Lagrange multipliers, "π_ℓ". This manipulation is demonstrated by R. J. Clasen (C-3). These equations are:

$$\sum_{\ell=1}^{M_t} r_{j\ell}\pi_\ell = S_j \qquad \text{(II-25)}$$

for $j=1,2,\ldots M_t$

for $\ell=1,2,\ldots M_t$

where $r_{j\ell} = \sum_{i=1}^{N_t} d_i^{-1} a_{j\ell} a_{\ell i} Y_i$

and $S_j = b_j + \sum_{i=1}^{N_t} a_{ji} Y_i (\ln Y_i + d_i^{-1} C_i) \quad j = 1,2,\ldots M_t$.

This set of M_t equations are solved simultaneously, and the estimates of "π_i" is substituted in equation (II-24) to obtain current estimates of "X_i". These estimates are then substituted as the initial estimates "Y_i" for the next iteration.

II.5 FIRST ORDER METHOD

The First Order method is an iterative procedure consisting of the following sequence:

(i) The Lagrange multipliers are calculated based on prior estimates of the mole numbers of the species.

(ii) The change in the mole number estimates is calculated from the new estimates of the multipliers.

For the chemical equilibrium problem, the equations are of similar form to those presented in a previous section, while their exact form can be found in Clasen (C-3). Also, for this problem, a convergence promotion technique and a set of convergence tests to terminate the search have been programmed.

Convergence is promoted by introducing a variable stepsize between iterations. The difference between the present and prior estimate of the mole numbers for each species is given by the following expression:

$$\theta_i = X_i - Y_i \quad . \tag{II-26}$$

for $i = 1,2,.....N_t$

The directional derivative of the system free energy in the direction of these deviations ($\theta_1, \theta_2, ..., \theta_{N+1}$), at the present estimates is calculated by the formulation as derived by Shapiro and Shapley (S-4), (i.e. Theorem 8.11):

$$\sum_{i=1}^{N_t} \theta_i \left(C_i + \ln \left(Y_i/\overline{Y_k}\right)\right). \tag{II-27}$$

The iteration is terminated if this quantity is not negative. Passing this test, a second test is based on the following convergence error:

$$"\varepsilon" = \sqrt{\frac{1}{N_t} \sum_{i=1}^{N_t} \left(\frac{\theta_i}{Y_i}\right)^2} \qquad \text{(II-28)}$$

If "ε" is less than some tolerance limit (set in this present work as $\text{TOL1}_{v} = 0.01$), the procedure is also terminated. Should these tests fail, then a new stepsize and direction is chosen. First, the ratio $-Y_i/\theta_i$ is determined for each θ_i less than zero, and the minimum value of this set is determined. This value is then compared to 1 and the lesser of the two chosen as the estimate of the stepsize factor "λ". A new estimate for the mole number is given based on the stepsize factor and deviation between estimates as shown by:

$$Z_i = Y_i + \lambda\theta_i. \qquad \text{(II-29)}$$

for $i = 1,2,\ldots.N_t$

The directional derivative of the system free energy is then determined at Z_i in the direction of the deviations (θ_1, θ_2, ..., θ_{N2}). Each component of this derivative is tested in order to determine if its value is less than or equal to zero, i.e.,

$$(\theta_i\,(C_i + \ln\,(Z_i/Z_k)) \leq 0). \qquad \text{(II-30)}$$

If the component is positive, the stepsize "λ" is reduced and the above step repeated until the test is successful. For the next iteration, Z_i now becomes the initial estimate of the mole numbers. The iteration is repeated until one of the two convergence tests is satisfied.

II.6 SECOND ORDER METHOD

The essential modification for the Second Order method is that the primary element estimated at each iteration has been changed from the mole number to the Lagrange multiplier. The last estimate of the multipliers made in the First Order method serve as the initial estimate. The values for the multipliers are then substituted into equation (II-22) to evaluate X_i from the direct rather than linear form. These estimates of the mole numbers usually fail to satisfy the mass balance constraints. The resulting deviation is characterized by:

$$G_\ell = B_\ell - \sum_{i=1}^{N_t} a_{\ell i} X_i . \qquad \text{(II-31)}$$

for $l = 1,2,\ldots M_t$

The true value of the multiplier is now represented by a prior estimate "λ_ℓ" and an error term "$\Delta\lambda_\ell$" combined in the following manner:

$$\pi_\ell = \lambda_\ell + \Delta\lambda_\ell . \qquad \text{(II-32)}$$

for $\ell = 1,2,\ldots M_t$

The problem now becomes one of determining the stepsize "$\Delta\lambda_i$" as a function of the deviations found in constraint equations.

The rate of change of the constraint error with respect to the value of the multiplier is represented by:

$$\frac{\partial G_j}{\partial \lambda_\ell} = - \sum_{i=1}^{N_t} a_{ji} \frac{\partial X_i}{\partial \lambda_\ell} . \qquad \text{(II-33)}$$

Substituting the nonlinear function (equation II-22) for "X_i", the partial differential becomes:

$$\frac{\partial G_j}{\partial \lambda_\ell} = - \sum_{i=1}^{N_t} a_{ji}\, d_i^{-1}\, X_i\, a_{\ell i} = - r_{\ell j} . \qquad \text{(II-34)}$$

The full differential is represented by:

$$dG_j = + \sum_{\ell=1}^{M_t} \frac{\partial G_j}{\partial \lambda_\ell}\, d\lambda_\ell = - \sum_{\ell=1}^{M_t} r_{\ell j}\, d\lambda_\ell . \qquad \text{(II-35)}$$

for $j = 1,2,3,\ldots M_t$

If the magnitude in both the constraint error and the multiplier error are sufficiently small in order that the rate of change:

$$\partial G_j / \partial \lambda_\ell$$

can be assumed constant, then by assuming:

$$dG_j = - G_j \quad \text{and} \quad d\lambda_\ell = \Delta\lambda_\ell ,$$

and substituting one obtains:

$$G_j = \sum_{\ell=1}^{M_t} r_{\ell j}\, \Delta\lambda_\ell . \qquad \text{(II-36)}$$

for $j = 1,2,\ldots M_t$

These M_t equations are solved simultaneously to obtain the constraint errors:

$$\Delta\lambda_1,\ \Delta\lambda_2,\ \ldots\ \Delta\lambda_{M_t} .$$

A convergence test is performed by:

(i) selecting the multiplier error of largest absolute value, i.e.,

$$P = \underset{j=1}{\overset{M_t}{\mathrm{MAX}}} \, /\Delta\lambda_j/$$

(ii) comparing this value to a tolerance limit (i.e., in this work TOL2 $= 10^{-5}$).

Should this test fail, a new stepsize is calculated as the product of the multiplier error and a factor "Q", where Q is either the minimum argument of the reciprocal of P or 1. This stepsize factor is used to prevent the multiplier from increasing excessively on one iteration, and thus resulting in an overshoot of the correct value. To prevent endless iterations, due to the selection of too small a tolerance limit, the iteration is also terminated if "P" should increase from the previous iteration. In this situation the tolerance limit had been selected at a level lower than the round—off error resulting from the computer calculations.

II.7 REVIEW OF ION ACTIVITY COEFFICIENT EQUATIONS

Debye and Hückel (D-6) put forth the first quantitative treatment of the electrostatic interaction between ions in 1923. Their equation, referred to as the Debye and Hückel limiting law (see Table 29), states that the activity coefficient is a function of the solvent temperature, dielectric properties, and the solute concentration and valency for dilute electrolytes. This equation has, as a model of a simple electrolyte, assumed that the ions acted as rigid, charged spheres in a solvent of constant dielectric properties and whose interaction could be predicted by Coulomb's law. This equation was further modified to account for the influence of the ions' size resulting in the extended form. The range of applicability was extended from $10^{2.3}$ moles/litre to 0.1 moles/litre by this correction. Again, application was intended for a simple electrolyte. This equation has the disadvantage of requiring knowledge of a parameter (i.e., a mean ionic diameter) which, in general, is lacking. Also, it is unclear what value this parameter should assume in an electrolyte made up of several salts.

For the wastewater model, a general equation suitable for several different mixed electrolytes was desired. The Davis equation (D-5) appeared as a reasonable choice. This equation is empirical with respect to the coefficients,

TABLE 29

ION ACTIVITY COEFFICIENT RELATIONSHIPS

Equation	
Debye-Hückel	$\log^{*} \gamma = -AZ_i\sqrt{I}$
Extended Debye-Huckel	$\log \gamma = -\dfrac{AZ_i^2\sqrt{I}}{1 + Ba\sqrt{I}}$
Davis	$\log \gamma = -.5\,Z_i^2\left(\dfrac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)$
Guntelberg	$\log \gamma = -AZ_i^2\left(\dfrac{\sqrt{I}}{1+\sqrt{I}}\right)$

where:

(i) $A = 1.82 \times 10^6\,(\varepsilon T)^{2/3}$ and ε = dielectric constant of pure solvent and "T" is solution temperature in degrees Kelvin (for water @ 25°C, $A = 0.5$),

(ii) $B = 50.3\,(\varepsilon T)^{-1/2}$ (for water @ 25°C $B = 0.33$),

(iii) a - mean ion diameter,

(iv) Z_i - charge of ion species "i",

(v) "I"-the ionic strength is defined as

$I = 1/2\,\Sigma\;C_i\,Z_i^2$,

(vi) C_i - is the ion concentration in moles per litre.

---

*Refers to logarithm to the base 10.

though the general form is similar to the relationship derived by Debye and Hückel. For the want of something better, at temperature and for solvents other than which this initial constant of 0.5 was determined (i.e., water at 25°C), the Debye and Hückel coefficient is substituted. Davis has compared the predictions of his equation to activity coefficients previously reported for simple uni-univalent, bi-univalent, uni-bivalent, and tri-univalent electrolytes up to 0.1 moles/litre in ionic strength, (i.e., 90 separate cases is all). He observed a maximum deviation of 2 percent from the experimental values reported. As the equation is empirical, only the concentrations of the ion species are required. The upper limit of ionic strength to which this equation is valid is almost five times greater than that which can be expected for typical wastewater. This statement is based upon the ionic strength found for the annual, average concentration of 19 cations and 10 anions found in the influent and effluent of the Hyperion Sewage Treatment Plant (B-2). Values of 0.022 and 0.0201 were calculated for the influent and effluent respectively.

Before the coefficients calculated from the Davies equation can be applied, a conversion is necessary from the molar to mole fraction concentration scales. As shown by Denbigh (D-9), this relationship is derived by equating the expressions of chemical potential for each scale. This is valid because the chemical potential is independent of the concentration scale. Thus, by equating expressions one obtains:

$$\mu^o_{XMF} + RT\ \ell n\ \gamma_{XMF}\ \hat{X} = \mu^o_c + RT\ \ell n\ \gamma_c\ c \qquad \text{(II-37)}$$

where μ^o represents the Gibbs chemical potential at constant temperature and pressure,

c is the molar concentration.

Upon rearrangement:

$$RT\ \ell n\left(\frac{\gamma_{XMF}\ \hat{X}}{\gamma_c\ c}\right) = \mu^o_c - \mu^o_{XMF} \qquad \text{(II-38)}$$

At high dilutions the activity coefficients approach unity and as the free energy constants are independent of concentration their difference is proportional to the logarithmic ratio of concentrations. At high dilutions, the concentration ratio is given by:

$$\frac{c}{\hat{X}} = 1000\ \rho o/Mo \qquad \text{(II-39)}$$

where ρo is the density of the solvent,

Mo is the molecular weight of the solvent.

The difference between chemical potential is equal to:

$$\mu^o_c - \mu^o_{XMF} = \ell n\left(\frac{Mo}{1000\ \rho o}\right) \qquad \text{(II-40)}$$

Upon substitution, the conversion is given by:

$$\frac{\gamma_{XMF}}{\gamma_c} = \frac{cMo}{1000\ \rho o}\ \hat{X} \qquad \text{(II-41)}$$

II.8 DESCRIPTION OF THE PARTIAL DERIVATIVE SUBROUTINES

The partial derivative package consists of these five subroutines:

(i) "JABY"
(ii) "LIST"
(iii) "PART"
(iv) "BJACOB"
(v) "CJACOB"

The partial derivatives can be calculated by using the subroutine "JABY" and the use of control data cards, as detailed in the Rand Memorandum (S-5) or by directly calling the other subroutines for a specific derivative. A brief description of the role of each subroutine will be given.

"JABY"(X) is a master control or executive program which directs the calling of other programs according to the type of dependent variable selected. Data cards of a specified format are required to relate the particular dependent variable (i.e., the species "i") and the independent variable (i.e., the component "ℓ") for which a value is desired. The value of the formal parameter and its corresponding argument is given in Table 30.

The subroutine "LIST" directs the reading of input data cards and the printing of output information. The program checks the data cards for incorrect spacing of

TABLE 30

FORMAL PARAMETER OF SUBROUTINE "JABY"

Formal Parameter Valve	Argument
0	Read and list data cards
1	Select the mole number, mole sum and pH as dependent variables
4	Logarithmic equivalent of above
2	Select mole fraction and pH as the dependent variable
5	Logarithmic equivalent of above
3	Select the mole sum and pH as a dependent variable
6	The logarithmic equivalent of above

information and prints this data with the message "illegal". Only 25 sets of variables may be entered in the present set of dimensions. However, in the place of a particular compartment substance and/or component name as an independent variable, the terms "ALL" or "MANY" may be substituted. The former term causes the printing of all partial derivatives of that type (independent variable), while the latter selects only those which result in a nondegenerate value (i.e., the variable has a nonzero value). Compartments for which no output information is wanted may be suppressed.

"PART" is the function statement which calculates the partial derivatives. It is normally called by "JABY". This function statement has five formal parameters: "PART"(KDEP, JNUM, KIND, NCOL, NROW). The first and third formal parameters referred to the type of dependent and independent variables, respectively. Their value and argument is shown in Table 31. The second parameter refers to either the species number or to the negative of the compartment number for the dependent variable. The last two parameters refer either to the species number and/or row number required to define the independent variable. If only one number is required, the other is set to zero. Before computation can begin, a matrix (stored as the array "R") must be inverted. This operation is performed by the subroutine "ARITH" when the common variable "MARITH" is set to zero. Thus, a call statement to the function "PART" must be proceeded by a call

TABLE 31

FIRST AND THIRD FORMAL PARAMETERS OF FUNCTION "PART"

First		Third	
Value	Argument	Value	Argument
(Dependent Variable)		(Independent Variable)	
1	Mole number	2	component
4	logarithm of above	3	stoichiometric coefficient
2	mole fraction	4	free energy constant
5	logarithm of above	5	exponential of free energy constant
3	mole sum of compartment	6	sum of the products of the components and their stoichiometric coefficients for species "i"
6	logarithm of above		
-1	pH in a compartment		
-2	logarithm of above		

for the subroutine "ARITH".

The other two function statements are "BJACOB (NROW, JNUM)" and "CJACOB (JNUM, NCOL)." The first calculates the partial derivative of the species "JNUM" with respect to the component "NROW". The second calculates the value of the partial derivative of the species "JNUM" with respect to the free energy value of the species "NCOL". Again, a call statement to the subroutine "ARITH" must proceed.

Subroutine "PHSOLVE" simulates an acid-base titration of the chemical system. Increments of acid or base are estimated which when added to the systems cause the pH value in a compartment to reach a specified level at equilibrium. Based on the Newton Raphson Method, these increments are determined by dividing the pH error by the partial derivative of pH taken with respect to the appropriate components. The pH error is the difference between the specified level and that value calculated at the present initial conditions. A positive deviation indicates additional hydroxide ion is required, while a negative value-the hydrogen ion. A counter ion, sodium or chloride, is also added in equimolar quantities to maintain charge neutrality in the system. In the component list, the hydrogen or hydroxide ions, are normally specified. The partial derivative of pH with respect to the acid or base is calculated as the sum of the derivatives of one of these ions and its counter ion. Thus:

$$\frac{\partial pH}{\partial HCl} = \frac{\partial pH}{\partial H^+} + \frac{\partial pH}{\partial Cl^-} \quad \text{or} \quad \frac{\partial pH}{\partial NaOH} = \frac{\partial pH}{\partial Na^+} + \frac{\partial pH}{\partial OH^-} \quad . \qquad \text{(II-42)}$$

and for a negative pH error:

$$\Delta HCl = \Delta pH \Big/ \frac{\partial pH}{\partial HCl} \qquad \text{(II-43)}$$

or for a positive pH error:

$$\Delta NaOH = \Delta pH \Big/ \frac{\partial pH}{\partial NaOH} \quad . \qquad \text{(II-44)}$$

The addition is made to the component list, the equilibrium problem resolved, and the resulting pH value compared to that level originally specified. Deland (D-8) presented a computer program employing this procedure.

For the chemical systems modelled in this work, the estimation procedure proved unsatisfactory. Frequently, the increments of acid or base were overestimated. This meant more iterations were needed to reach a solution, and an excess of hydrogen and hydroxide ions were added to the system. As an excess of these ions readily combine to form water, the effect is a dilution of the other species' concentrations.

This problem is overcome by the use of a variable step-size. For example, in the case of acid addition, should the newly calculated pH value lie less than one-tenth of a unit below that specified, then the acid increment is halved and the problem resolved. Similarly for a base, overshoot by one-tenth of a pH unit above the required value results in the addition being halved. The increment is repeatedly halved until either the preceeding criterion is satisfied or the addition no longer results in an overshoot. At this point the iteration cycle begins once more. A new difference is calculated between the last pH value and the specified level and a new estimate of addition determined from the partial derivative. The program converges if either the difference between the pH levels is less than 0.02 units (in the present work) or if the chemical equilibrium problem has been solved a greater number of times than that specified by the iteration limit. In the latter case, an error message noting the difference between required and calculated pH values is printed.

This technique is programmed in the subroutine "PHSOLVE". The information needed by the subroutine is introduced by a formal argument whose parameters have the following values:

(i) "NAME" identifies the compartment in which the pH is to be specified,

(ii) "VALUE" is set at the specified pH level,

(iii) "LIM" is set to the maximum number of iterations permitted,

(iv) "IC" identifies if the problem is to be solved with (equals 2) or without (equals 1) corrections for ionic activity.

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II.9 ADDITIONAL MATHEMATICAL SYMBOLS FOR APPENDIX II

$a_{\ell i}$	constants used in the linear logarithmic problem
b_{ℓ}	
c_i	
d_i	
c	molar concentration
G_{ℓ}	error in mass balance equation
k_i	constant for Linear Programming Method
L	value of objective function in optimization problems
M	total number of components
Mo	molecular weight of solvent
N	total number of species
X_i	variable in the linear logarithmic problem
W_i	weighting factor in the Projection Method
Y_i	prior estimate of species' mole number
Y_k	prior estimate of the sum of moles
Z_i	projected mole number estimate in the next iteration (First Order Method)
ϵ	convergence error (First Order Method)
Π_{ℓ}	Lagrange Multiplier

θ_i	difference between estimated and true value of species' mole number
λ	stepsize factor (First Order Method)
λ_ℓ	prior estimate of Lagrange multiplies
$\rho\varrho$	solvent density
μ^o	chemical potential at standard state

APPENDIX III: PARAMETER ESTIMATION AND EXPERIMENTAL DESIGN

III.1 EXPRESSIONS USED IN THE PARAMETER ESTIMATION PROBLEM

An explanation of the criteria (equation (13) and (15)) used to determine estimates of the parameters (i.e. vector B) in the general multiresponse model shown by equation (12) in chapter III is presented. Two situations are considered, each with its own criterion. One is the case in which the errors associated with the observations are unknown, while in the other case the values of these errors are known.

In both situations, the following assumptions are made. The model is assumed to provide the correct response (i.e., $E(Y_{iu}) = N_i(X_u, B)$). The observations are considered to be random variables which are normally distributed. Therefore, the probability of Y_{iu} is defined by two parameters, its expected value (i.e., the model) and its variance σ_{ii}^{u}. The variance of Y_{iu} is a function of the random error ε_{iu}, given by:

$$E(\varepsilon_{iu}^2) = \sigma_{ii}^{u} \qquad \text{(III-1)}$$

the properties which these errors are assumed to have are:

$E(\varepsilon_{iu}) = 0$ all i, u,

$E(\varepsilon_{iu}, \varepsilon_{jv}) = 0$ all i, j, $v \neq u$,

$E(\varepsilon_{iu}, \varepsilon_{ju}) = \sigma_{ij}^{u}$, $i \neq j$.

The probability of a single observation is written as:

$$P[Y_{iu}/B,\ X_u,\ \sigma_{ii}^{u}] = \frac{1}{\sigma_{ii}^{u}\sqrt{2\pi}} \exp\left[-1/2\ \sigma_{ii}^{u}\ (Y_{iu} - N_i(X_u,\ B))^2\right], \qquad \text{(III-2)}$$

while the joint probability of a set of k observations for one experiment is written as: (III-3)

$$P[Y_u/B, X_u, \sigma^u_{ij}] = 2\pi^{-k/2}|\sigma^{ij}_u|^{\frac{1}{2}} \exp [-1/2 \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma^{ij}_u V^u_{ij}],$$

where $V^u_{ij} = (Y_{iu} - N_i(X_u, B))(Y_{ju} - N_j(X_u, B))$.

The term σ^{ij}_u is an element of the inverse covariance matrix of Y_u. As each experiment is assumed to be an independent event, the probability of all observations for a set of N_x experiments is the multiple product of the joint probabilities of the observations in each experiment. This is written as:

$$P[Y/B,X, \sigma^u_{ij}] = 2\pi^{-N_x/2} \prod_{u=1}^{N_x} |\sigma^{ij}_u|^{\frac{1}{2}} \exp [-1/2 \sum_{u=1}^{N_x} \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma^{ij}_u V^u_{ij}]$$

(III-4)

where Y is the matrix of all experimental observations,

X is the matrix of all the independent variables in N_x experiments.

The product of the pre-exponential terms are positive and represented by the factor "A".

The likelihood function of the parameters is equivalent to the probability density of the observations, except that the parameters become the random variables and the observations are fixed. Thus: (III-5)

$$L(B/X, Y, \sigma^u_{ij}) = A \exp (-1/2 \sum_{u=1}^{N_x} \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma^{ij}_u V^u_{ij})$$

Because the summation in the exponent yields a positive value, the maximum likelihood estimates of the parameters are those estimates which minimize this value. This summation is the general form of the search criterion for the parameter estimation problem (i.e., equation (15)) in which the covariance is not constant for each experiment and is known.

For the situation in which the covariance is not known, it is assumed to be constant for all experiments. Therefore the script "u" may be removed by an earlier summation and the likelihood function for the parameter becomes:

$$L(\beta/X,Y,\sigma^{ij}) = A \exp\left(-1/2 \sum_{i=1}^{k} \sum_{j=1}^{k} \sigma^{ij} V_{ij}\right) \tag{III-6}$$

where (i) $V_{ij} = \sum_{u=1}^{N_x} V_{ij}^{u}$,

(ii) $A = 2\pi^{-\frac{1}{2}N_x k} \left| \sigma^{ij} \right|^{\frac{1}{2}N_x}$.

Box and Draper (B-16) assumed the following prior distribution for the parameters β and the elements of the inverse covariance matrix. That is:

$$p(\beta) \propto d\beta , \tag{III-7}$$

$$p(\sigma^{ij}) = \left| \sigma^{ij} \right|^{-\frac{1}{2}(k+1)} . \tag{III-8}$$

With these functions, they integrated out the covariance terms from the likelihood function (equation (III-6)) with the result that:

$$L(\beta/Y) = C \left| V_{ij} \right|^{-\frac{1}{2}N_x} \tag{III-9}$$

where

$$C = \left\{ \int \left| V_{ij} \right|^{-\frac{1}{2}N_x} d\beta \right\}^{-1} \tag{III-10}$$

is a normalizing constant. Thus the parameter estimate is given by the minimum value of the determinant (i.e., criterion A-equation (13)).

As discussed in section 1 of chapter III, Box (B-18) made a distinction between errors in the actual measured quantities, which he designated as prime, and effective errors. The latter group includes the effect of the uncertainties in specifying the levels of the independent variables upon the total error in the measured response. The effective error for the i-th response is given by:

$$\varepsilon_{iu} = e_{iu} + \sum_{\ell=1}^{L} e_{\ell u} C_{iu\ell} \qquad \text{(III-11)}$$

where in the u-th experiment:

(i) e_{iu} is the prime error in the actual measured quantity,

(ii) $e_{\ell u}$ is the prime error in the level of the independent variable,

(iii) $C_{iu\ell}$ is the partial derivative of the model for the i-th response with respect to the ℓ-th independent variable,

(iv) ε_{iu} is the effective error of the i-th response.

The prime errors are assumed to have the following properties:

$E(e_{iu}) = 0$ all i,

$E(e_{iu}, e_{ju}) = 0$ all i, j,

$E(e_{iu}, e_{jv}) = 0$ all i, j, $u \neq v$.

It follows that effective errors have the properties of:

$E(\varepsilon_{iu}) = 0$ all i,

$E(\varepsilon_{iu}, \varepsilon_{jv}) = 0$ all i, j, $u \neq v$.

The estimates of the effective variance for the i-th response is given by:

$$\sigma^u_{ii} = E(e^2_{iu}) + \sum_{\ell=1}^{L} E(e^2_{\ell u})\, C^2_{iu\ell} , \qquad \text{(III-12)}$$

and the covariance between the i-th and j-th response is:

$$\sigma^u_{ij} = \sum_{\ell=1}^{L} E(e^2_{\ell u})\, C_{iu\ell}\, C_{ju\ell} . \qquad \text{(III-13)}$$

The following estimates of the errors in the levels of the independent variables were made. These errors were assumed to be constant for every experiment. The estimates were used in the experiments described in sections 3, 4 and 5 of chapter IV. In the experiments, the level of each independent variable was set by adding an aliquot from a stock solution to a dilute one. The error estimates were based upon the accuracy with which the concentration of the stock solution was known and the aliquot was measured. These error estimates are:

(i) initial lanthanum concentration--10^{-5} moles,

(ii) initial phosphate concentration--10^{-6} moles,

(iii) initial carbonate concentration--10^{-5} moles,

(iv) initial acid concentration--10^{-6} moles,

(v) initial base concentration--10^{-5} moles.

The multiple correlation coefficient is another way to judge parameter estimates. The coefficient is defined as the ratio of the variance removed by the model over the variance in the observations themselves. This ratio is calculated by the following expression for each response:

$$\hat{\rho}_i^2 = 1 - \frac{\sum_{u=1}^{N_x} \sigma_u^{ii} V_{ii}^u}{\sum_{u=1}^{N_x} \sigma_u^{ii} (Y_{iu} - \overline{Y}_i)^2} \qquad \text{(III-14)}$$

where (i) $\overline{Y}_i$ is the average value of the i-th response over all N_x experiments,

(ii) $\hat{\rho}_i$ is the multiple correlation coefficient for the i-th response.

III.2 AN ALGORITHM OF THE COMPUTER SUBROUTINES USED IN THE PARAMETER ESTIMATION PROBLEM

The computer subroutines which are used with "CHEMIST" to estimate the free energy parameters are described here. The flow of the computations is illustrated in Figure 27. Listings of the four subroutines are provided in section 1 of Appendix VI.

The main program "TST" reads in the data required for parameter estimation and to define the chemical system. The latter set is introduced by a call to the subroutine "INPUT" and the use of the data control card option. The search is initiated by a call to the subroutine "SIMPLEX". After the search is completed, control is returned to "TST". The model predictions are now calculated with the best parameter estimates by a call to the subroutine "MODEL". A print control variable is also set which causes "MODEL" to print the concentrations of each species in every phase and the values of the partial derivatives for each experiment. Returning to "TST", the residuals ~~and~~ their root mean squares are calculated. The information printed by "TST" is:

(i) the initial, observed and the predicted concentrations of the dependent variables,

(ii) the root mean squares of the residuals of each response,

(iii) plots of the residuals versus the predicted response.

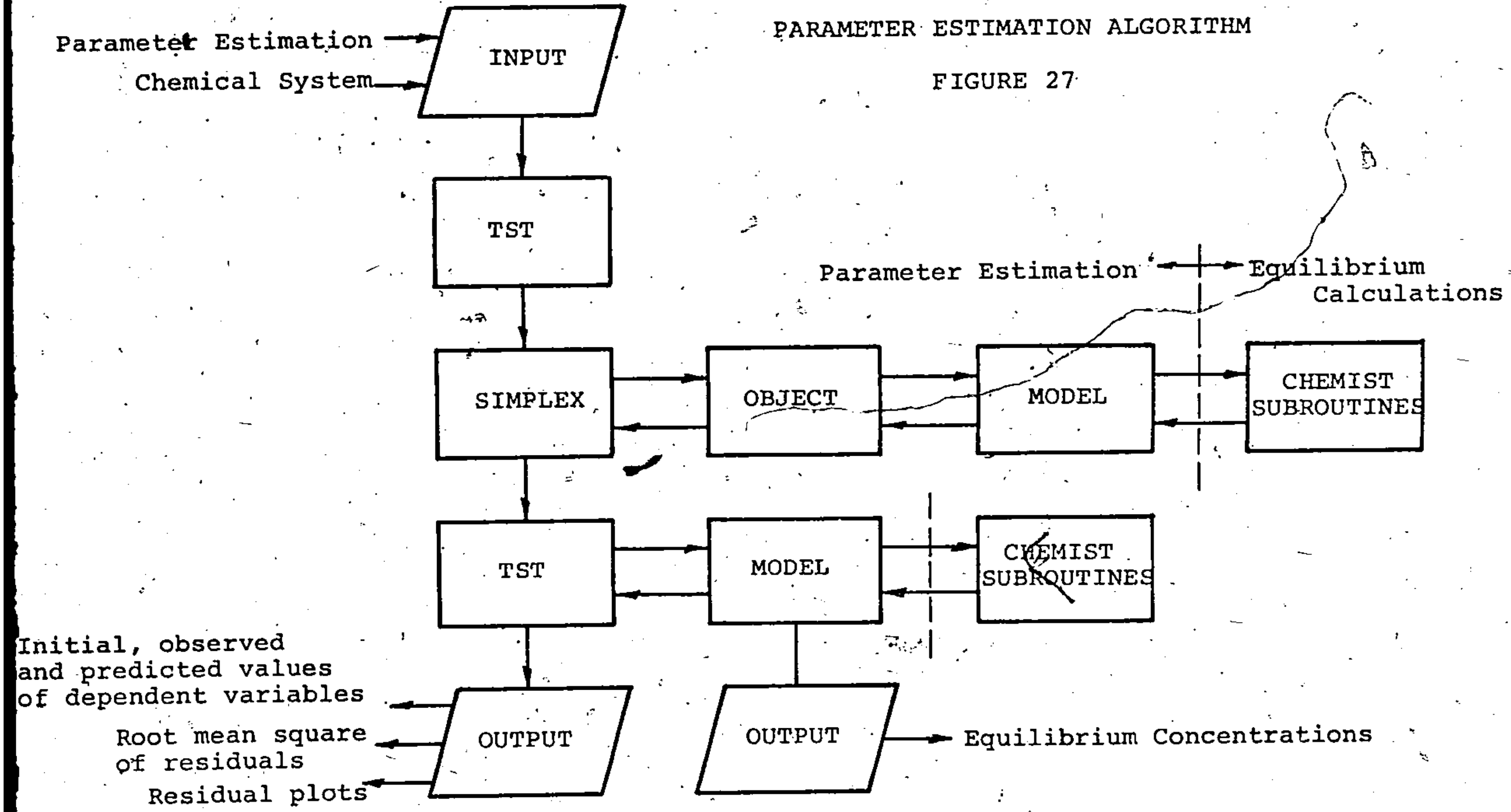
The subroutine "SIMPLEX" contains the Nelder and Mead algorithm (N-1, H-5) for the "Flexible Simplex" search. Control is maintained in this subroutine during the search for parameter estimates. The value of the search criterion or objective function for each set of parameter values is obtained by a call to the subroutine "OBJECT".

The objective function is programmed in the subroutine "OBJECT". The model predictions needed for this function are obtained by a call to the subroutine "MODEL". Information concerning the values of the independent variables (i.e., number of moles of each component) is transferred here from "TST" to "MODEL". The effective errors and the inverse of the covariance matrix is also calculated here.

The subroutine "MODEL" is the link between the parameter estimation routines and the "CHEMIST" subroutines. By calls to the appropriate subroutines, estimates of the species' concentrations at equilibrium (i.e., "CALL SOLVE"), and values for the partial derivatives (i.e., "CALL BJACOB" and "CALL CJACOB") are obtained. The subroutine is written in a general format that allows the calculation of the total concentration of an element in a phase and its corresponding partial derivatives for most chemical systems. The information needed with respect to species, component, and free energy parameter numbers for a particular chemical system is stored in data statements here.

PARAMETER ESTIMATION ALGORITHM

FIGURE 27



III.3 AN ALGORITHM OF THE COMPUTER SUBROUTINES USED TO DESIGN EXPERIMENTS

The computer subroutines which are used with "CHEMIST" to design experiments are described here. The order of the computation procedure is illustrated in Figure 28. Listings of the seven subroutines are provided in section 2 of Appendix VI.

The main program "TST", introduces the input data, initiates the search for experiments and prints the resulting information. Initial estimates of the independent variables are read in with their upper and lower constraints. Operating information specific to the search subroutines, (e.g., number of parameters to be estimated, permissible number of iterations, etc.) is introduced by a "BLOCK DATA" subroutine. The data needed to describe the chemical system is read in by a call to the subroutine "INPUT". The search for experiments is performed by the subroutine "MINI". After the experiments have been selected, control returns to "TST". A call to the subroutine "MODEL" via the subroutine "FUN" causes the calculation and printing of the equilibrium concentrations in the aqueous phase and the partial derivatives at the new experimental conditions. From subroutine "FUN", the covariance matrix and it's inverse for the predicted responses for each new experiment is also printed. Also, the value of the elements contributed by each experiment to the determinant of the design criterion are printed. The remaining output information is printed by "TST" and includes:

(i) the final selections of the independent variables,

(ii) the determinant of the design criterion, (i.e., the inverse of the parameter covariance matrix),

(iii) the reciprocal value of the determinant,

(iv) the predicted responses and number of moles of each solid phase for each experiment.

The subroutine "FUN" calculates the objective function for the search routines. In order to efficiently use the search routines, the design problem was transformed from one with constrainted variables to unconstrainted ones by the following equation:

$$x_i = g_i + (h_i - g_i)\sin^2 y_i \qquad \text{(III-15)}$$

for $i = 1, 2, \ldots n_t$

where x_i is the constrainted search variable,

y_i is the unconstrainted variable,

g_i is the lower bound,

h_i is the upper bound,

n_t is the number of variables.

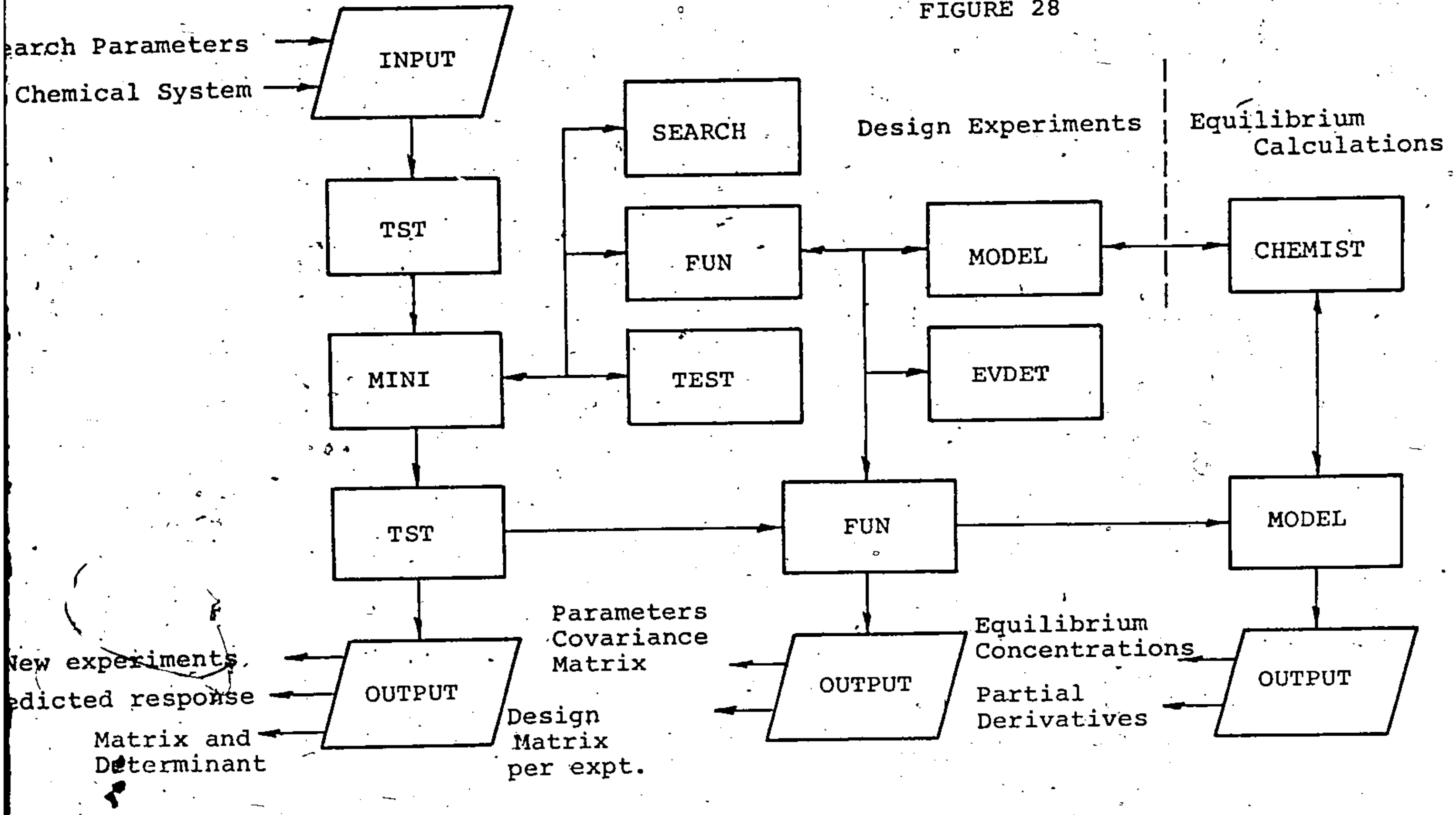
The contributions of the experiments already performed to the design criterion are stored in this subroutine by Data statements. Estimates of the effective errors in the covariance matrix of y_u are made in the same manner used in the parameter estimation problem. Values of the predicted responses and partial derivatives for each new experiment are obtained from the subroutine "MODEL". The value of the determinant is calculated by the subroutine "EVDET". The solution technique used in "EVDET" is based upon the method of elimination as outlined by Lapidus (L-1). The progress of the search for new experiments is monitored by printing the current search variables and the value of the design criterion at each step.

The subroutine "MODEL" performs the same role as before in the parameter estimation problem. The calculations from "CHEMIST" are transformed to a convenient form (e.g., calculating the partial derivative of a response from the derivatives that belong to a set of species), and then transferred to the subroutine "FUN".

Three subroutines are used to carry out the search based on Powell's algorithm. Box (B-19) particularily favoured this method because it possesses quadratic convergence, (i.e., the property that the method will converge to the minimum of a quadratic function in a finite number of steps). Though the design criterion is not a strict quadratic function it was found that this method converged more rapidly than others. The search is directed by the subroutine "MINI". "SEARCH" is an auxiliary subroutine used to determine the optimum stepsize in the direction of each parameter. This program is based upon the method of Golden Sections. The third subroutine "TEST" contains a set of convergence criteria used to terminate the search procedure. More detail concerning these subroutines is given by Himmilblau (H-6).

EXPERIMENTAL DESIGN ALGORITHM

FIGURE 28



APPENDIX IV: EXPERIMENTAL INFORMATION

IV.1 LA - PO4 - CO3 - H2O SYSTEM

TABLE 32

```
*****************************************************************************

               MATRIX OF SPECIES, COMPONENTS, AND REACTIONS

        (FREE ENERGY CONSTANTS EVALUATED AT 25 DEGREES CENTIGRADE)

 SPECIES  FREE ENERGY  -  STOICHIOMETRIC COEFFICIENTS
          CONSTANTS    :  AND COMPONENTS
*****************************************************************************

 AQUEOUS SOLUTION (COMPARTMENT - LIQUID)

   H+                    1.0  H+
   NA+                   1.0  NA+
   K+                    1.0  K+
   OH-                   1.0  OH-
   CL-                   1.0  CL-
   H2O    -40.2571       1.0  H+     1.0   OH-
   LA+3                  1.0  LA+3
   LAOH   -12.2327       1.0  LA+3   1.0   OH-
   HPO4   -32.3939       1.0  H+     1.0   PO4-3
   PO4-3                 1.0  PO4-3
   H2PO4  -52.9824       2.0  H+     1.0   PO4-3
   CO3-2                 1.0  CO3-2
   H2CO3  -46.4382       2.0  H+     1.0   CO3-2
```

```
      NACO3--6.9387       1.0   NA+    1.0   CO3-2
      NAHCO3-31.2367      1.0   NA+    1.0   H+     1.0   CO3-2
      HCO3- -27.7979      1.0   H+     1.0   CO3-2
   ORTHOPHOSPHATE PRECIPITATE (COMPARTMENT - PHOSPHATE)

       LAPO4  S            1.0   LA+3  1.0   PO4-3

   LANTHANUM CARBONATE PRECIPITATE (COMPARTMENT - CARBONATE)

        LACO3  S            2.0   LA+3  3.0   CO3-2

   LANTHANUM HYDROXIDE PRECIPITATE (COMPARTMENT - HYDROXIDE)

        LAOH3  S             1.    LA+3   3.    OH-

*************************************************************************************

             (FREE ENERGY CONSTANTS EVALUATED AT  5 DEGREES CENTIGRADE)
*************************************************************************************

    AQUEOUS SOLUTION (COMPARTMENT - LIQUID)


         H2O    -41.9588     1.    H+     1.0   OH-
         H+                  1.0   H+
         NA+                 1.0   NA+
         K+                  1.0   K+
         OH-                 1.0   OH-
         CL-                 1.    CL-
         LA+3                1.0   LA+3
         LAOH   -12.2327     1.0   LA+3   1.0   OH-
```

```
PO4-3               1.0   PO4-3

HPO4   -32.8776     1.0   H+      1.0   PO4-3

H2PO4  -53.6569     2.0   H+      1.0   PO4-3

CO3-2               1.0   CO3-2

HCO3-  -28.3249     1.0   H+      1.0   CO3-2

H2CO3  -47.3473     2.0   H+      1.0   CO3-2

NACO3--6.9387       1.0   NA+     1.0   CO3-2

NAHCO3-31.2367      1.0   NA+     1.0   H+      1.0   CO3-2


ORTHOPHOSPHATE PRECIPITATE (COMPARTMENT - PHOSPHATE)


   LAPO4 S            1.0   LA+3   1.0   PO4-3


LANTHANUM CARBONATE PRECIPITATE (COMPARTMENT - CARBONATE)


   LACO3 S            2.0   LA+3   3.0   CO3-2


LANTHANUM HYDROXIDE PRECIPITATE (COMPARTMENT - HYDROXIDE)


   LAOH3 S             1.   LA+3    3.   OH-

*****************************************************************************************

        $ FREE ENERGY PARAMETERS TO BE EVALUATED
```

TABLE 33

La - PO_4 - CO_3 - H_2O SYSTEM
INITIAL AND FINAL CONDITIONS

A. First Twelve Experiments at 25°C

	Lanthanum (mgLa/1)	Orthophosphate (mgP/1)	Carbonate (mgCO$_3$/1)	Hydroxide (mgNaOH/1)
Initial	103.	30.8	174.7	71.8
Final	N.R.*	8.6	177.3	8.798**
	68.7	30.9	179.7	59.9
	N.R.	18.1	177.3	8.767**
	35.7	30.9	179.7	51.9
	N.R.	25.1	177.3	8.860**
	138.3	23.1	179.2	75.6
	N.R.	.02	155.8	8.711**
	68.7	23.2	179.7	51.9
	N.R.	9.3	177.3	8.790**
	34.4	23.2	179.9	40.
	N.R.	15.9	178.3	8.518**
	138.3	15.4	179.2	71.6
	N.R.	.05	137.2	8.518**
	103.	15.5	174.7	55.8
	N.R.	.04	156.7	8.660**
	34.4	15.5	179.9	32.
	N.R.	8.64	179.3	8.758**
	125.6	7.3	170.7	64.4
	N.R.	.11	107.8	9.111**
	103.0	7.7	174.7	51.8
	N.R.	.07	142.1	8.428**
	68.7	7.7	179.7	75.8
	N.R.	.08	166.5	9.830**

*N.R. = not recorded.

**Final pH

B. Six Experiments at 25°C

	Lanthanum (mgLa/1)	OrtHophosphate (mgP/1)	Carbonate (mgCO3/1)	Hydroxide (mgNaOH/1)
Initial	143.0	16.3	59.3	72.8
Final	N.R.*	< .003	18.7	7.091**
	105.4	9.9	57.3	52.1
	N.R.	< .003	25.7	8.201**
	133.7	23.2	274.5	79.2
	N.R.	.066	277.	8.902**
	70.17	18.0	59.3	50.4
	N.R.	8.15	56.9	8.360**
	111.2	32.2	178.0	71.2
	N.R.	7.34	178.6	8.443**
	104.6	32.2	296.7	72.8
	N.R.	9.12	293.4	8.719**

C. Five Experiments at 5°C

	Lanthanum (mgLa/1)	OrtHophosphate (mgP/1)	Carbonate (mgCO3/1)	Hydroxide (mgNaOH/1)
Initial	119.2	30.4	304.7	88.
Final	N.R.*	5.90	298.2	9.201**
	95.3	21.8	298.7	64.
	N.R.	2.61	297.6	8.894**
	146.8	25.5	59.7	76.
	N.R.	.26	35.7	7.281**
	59.6	14.7	298.7	52.
	N.R.	2.94	297.6	9.298**
	109.	16.9	59.7	56.
	N.R.	.14	38.2	7.648**

D. Four Experiments at 5°C

	Lanthanum (mgLa/l)	Orthophosphate (mgP/l)	Carbonate ($mgCO_3/l$)	Hydroxide (mgNaOH/l)
Initial	107.1	21.3	58.7	56. **
Final	1.0	.47	57.7	7.779
	138.4	21.9	60.3	70.2 **
	1.0	.016	34.3	7.975
	171.2	21.9	60.3	86.2 **
	1.1	< .003	18.8	7.532
	213.7	21.7	59.7	98.12 **
	15.2	< .003	6.1	7.625

E. Three Experiments at 25°C

Initial	77.7	13.1	93.9	53.2 **
Final	.06	.046	88.6	8.836
	142.	1.53	14.4	57.6 **
	52.7	< .003	5.3	8.457
	72.4	16.14	361.2	118.4 **
	N.R.*	2.61	360.6	9.518

F. Three Experiments at 25°C

Initial	69.9	14.4	366.0	86.4 **
Final	N.R.*	.93	361.8	8.977
	57.3	18.1	366.0	92.8 **
	N.R.	.31	360.3	9.029
	71.1	15.9	351.3	73.6 **
	N.R.	1.09	346.3	8.835

IV.2 LA - P3010 - H2O SYSTEM

TABLE 34

```
**************************************************************************************

                     MATRIX OF SPECIES, COMPONENTS, AND REACTIONS


               (FREE ENERGY CONSTANTS EVALUATED AT 25 DEGREES CENTIGRADE)


   SPECIES   FREE ENERGY      STOICHIOMETRIC COEFFICIENTS
              CONSTANTS       AND COMPONENTS
**************************************************************************************


AQUEOUS SOLUTION (COMPARTMENT - LIQUID)


     H+                     1.0   H+
     OH-                    1.0   OH-
     CL-                    1.0   CL-
     H2O     -40.2571       1.0   H+      1.0   OH-
     LAOH    -12.2327       1.0   LA+3    1.0   OH-
     LA+3                   1.    LA+3
     LAPOL    $             1.    LA+3    1.    POLY
     LAHPOL   $             1.    H+      1.    POLY    1.   LA+3
     H3POLY-53.5818         3.    H+      1.    POLY
     H2POLY-44.2715         1.    POLY    2.    H+
     HPOLY  -25.2903        1.    H+      1.    POLY
     POLY                   1.    POLY
     NAPOLY-10.4616         1.    NA+     1.    POLY
```

```
LANTHANUM TRIPOLYPHOSPHATE PRECIPITATE  (COMPARTMENT - POLY - P)

    LAPOLY  $            5.   LA+3   3.   POLY

*************************************************************************************

        (FREE ENERGY CONSTANTS EVALUATED AT  5 DEGREES CENTIGRADE)

*************************************************************************************


 AQUEOUS SOLUTION (COMPARTMENT - LIQUID)

     H+                  1.0   H+
     OH-                 1.0   OH-
     NA+                 1.0   NA+
     NA+                 1.0   NA+
     CL-                 1.0   CL-
     H2O   -41.9588      1.0   H+    1.0   OH-
     LAOH  -12.2327      1.0   LA+3  1.0   OH-
     LA+3                1.    LA+3
     LAPOL  $            1.    LA+3  1.    POLY
     LAHPOL  $           1.    H+    1.    POLY   1.   LA+3
     H3POLY-51.2941      3.    H+    1.    POLY
     H2POLY-42.2387      1.    POLY  2.    H+
     HPOLY -25.3712      1.    H+    1.    POLY
     POLY                1.    POLY
     NAPOLY-10.4616      1.    NA+   1.    POLY

 LANTHANUM TRIPOLYPHOSPHATE PRECIPITATE  (COMPARTMENT - POLY - P)

     LAPOLY  $           5.   LA+3   3.   POLY
```

```
*****************************************************************************

$  FREE ENERGY PARAMETERS TO BE EVALUATED
```

TABLE 35

La - P_3O_{10} SYSTEM
INITIAL AND FINAL CONDITIONS

A. Stage 1 - Six Experiments at 25°C

	Lanthanum (mg_{La}/l)	Tripolyphosphate (mg_P/l)	Acid (mg HCl/l)
Initial	35.0	11.7	.966
Final	4.4	.367	4.952**
	35.0	11.7	.459
	3.25	.345	4.988**
	69.9	22.7	1.958
	9.9	.661	4.348**
	69.9	34.3	4.887
	12.3	12.6	5.010**
	69.9	34.3	1.349
	19.4	14.3	5.962**
	103.	24.3	1.543
	14.4	.863	4.480**

B. Stage 2 - Three Experiments at 25°C

	Lanthanum (mg_{La}/l)	Tripolyphosphate (mg_P/l)	Acid (mg HCl/l)
Initial	68.9	24.6	2.042
Final	4.1	1.39	4.230**
	51.9	33.2	17.795
	29.2	24.9	3.660**
	42.4	35.2	7.585
	39.4	35.2	5.429**

C. Stage 3 — Two Experiments at 25°C

	Lanthanum (mgLa/l)	Tripolyphosphate (mgP/l)	Acid (mg HCl/l)
Initial	51.9	48.8	9.346**
Final	50.	47.3	5.800
	138.7	4.5	36.467**
	138.	3.35	3.561
	D. Six Experiments at 5°C		
Initial	35.0	11.7	.663**
Final	N.R.*	.845	5.040
	35.0	11.7	.352**
	N.R.	.423	5.289
	69.9	22.7	.615**
	N.R.	.863	5.120
	69.9	34.3	7.613**
	N.R.	18.6	5.255
	69.9	34.3	8.131**
	N.R.	21.2	6.570
	103.	34,3	0.772**
	N.R.	1.45	5.265

*N.R. = not recorded.

**Residual pH Value.

IV.3 LA - P2O7 - H2O SYSTEM

TABLE 36

```
*****************************************************************************

                 MATRIX OF SPECIES, COMPONENTS, AND REACTIONS

         (FREE ENERGY CONSTANTS EVALUATED AT 25 DEGREES CENTIGRADE)

SPECIES   FREE ENERGY       STOICHIOMETRIC COEFFICIENTS
          CONSTANTS         AND COMPONENTS
*****************************************************************************

AQUEOUS SOLUTION (COMPARTMENT - LIQUID)

     H+                     1.0   H+
     OH-                    1.0   OH-
     NA+                    1.0   NA+
     CL-                    1.0   CL-
     H2O    -40.2571        1.0   H+      1.0    OH-
     LA+3                   1.    LA+3
     LAOH   -12.2327        1.0   LA+3    1.0    OH-
     LAPYR S                1.    LA+3    1.     PYRO
     H3PYRO-55.2372         3.    H+      1.     PYRO
     H2PYRO-45.1448         1.    PYRO    2.     H+
     HPYRO -25.6809         1.    H+      1.     PYRO
     PYRO                   1.    PYRO
     NAPYRO-9.3095          1.    NA+     1.     PYRO
```

```
       KPYRO-9.3095        1.    K+      1.    PYRO

   LANTHANUM PYROPHOSPHATE PRECIPITATE (COMPARTMENT - PYRO - P)

       LAPYRO $            4.    LA+3    3.    PYRO

*************************************************************************************************

          (FREE ENERGY CONSTANTS EVALUATED AT  5 DEGREES CENTIGRADE)

*************************************************************************************************

   AQUEOUS SOLUTION (COMPARTMENT - LIQUID)

       H+                  1.0   H+
       OH-                 1.0   OH-
       NA+                 1.0   NA+
       CL-                 1.0   CL-
       H2O    -41.9588     1.0   H+      1.0   OH-
       LA+3                1.    LA+3
       LAOH   -12.2327     1.0   LA+3    1.0   OH-
       LAPYR $             1.    LA+3    1.    PYRO
       H3PYRO-52.3367      3.    H+      1.    PYRO
       H2PYRO-43.6752      1.    PYRO    2.    H+
       HPYRO  -24.8775     1.    H+      1.    PYRO
       PYRO                1.    PYRO

   LANTHANUM PYROPHOSPHATE PRECIPITATE (COMPARTMENT - PYRO - P)

       LAPYRO $            4.    LA+3    3.    PYRO

*************************************************************************************************
```

```
$ FREE ENERGY PARAMETERS TO BE EVALUATED
```

TABLE 37

La - P_2O_7 System

Initial and Final Condition

	Lanthanum (mgLa/l)	Pyrophosphate (mgP/l)	Acid (mgHCl/l)
A. Three Experiments at 25°C			
Initial	78.4	8.26	.304*
Final	50.5	.037	5.100
	78.4	16.02	.133*
	28.1	.018	5.453
	51.9	24.24	2.77*
	6.4	5.110	8.468
B. Three Experiments at 25°C			
Initial	44.5	12.45	4.340*
Final	7.8	.324	4.004
	35.8	16.52	2.440*
	5.05	6.695	8.185
	65.9	13.59	6.382*
	29.8	.997	3.844
C: Three Experiments at 25°C			
Initial	138.8	3.13	36.467*
Final	141.	2.675	3.520
	138.8	3.13	36.467*
	138.5	2.560	3.530
	138.8	3.13	36.467*
	141.	2.778	3.522

*Final pH

	Lanthanum (mgLa/l)	Pyrophosphate (mgP/l)	Acid (mg HCl/l)
	D. Four Experiments at 25°C		
Initial	66.7	32.41	4.157
Final	6.0	10.04	8.132*
	78.3	31.96	5.751
	.99	3.989	4.646*
	138.7	3.09	.536
	127.	.043	4.850*
	137.7	7.21	3.709
	.53	2.493	4.600*
	E. Three Experiments at 5°C		
Initial	44.5	12.45	5.589
Final	9.35	1.371	3.945*
	35.8	16.52	.547
	10.	7.799	8.705*
	65.9	13.59	7.679
	29.7	1.407	3.765*

---

*Final pH.

TABLE 38

$La - PO_4 - P_3O_{10} - P_2O_7 - CO_3^{=} - H_2O$ SYSTEM AT 25°C

	La	P_3O_{10}	PO_4 (mg/l)	CO_3	P_2O_7	pH	NaCl
Initial	75.6	3.7	12.	240.1	4.		146
Final	0.3	D.L.	.2	5.5	D.L.	6.370	
	75.6	3.7	12.	240.1	4.		146
	4.0	.094	1.1	55.5	.11	8.125	
	75.6	3.7	12.	240.1	4.		146
	6.5	0.50	3.3	269.	0.46	9.300	
	68.	7.3	8.	240.1	4.		146
	0.1	0.8	.15	9.	.02	6.626	
	68.	7.3	8.	240.1	4.		146
	3.9	.42	2.4	62.5	.60	8.258	
	68.	7.3	8.	240.1	4.		146
	7.	.55	2.	270.	1.98	9.543	
	60.5	11.0	4.	240.1	4.		146
	.55	.26	.45	5.5	.17	6.672	
	60.5	11.0	4.	240.1	4.		146
	9.6	3.28	1.95	55.	1.02	8.263	
	60.5	11.0	4.	240.1	4.		146
	10.7	3.77	2.3	265.5	2.33	9.522	

IV.5

TABLE 39

LANTHANUM PHOSPHATE PRECIPITATION IN WASTEWATER AT 25°C

	La	Ca	mg (mg/l)	Na	K	Cl	SO_4	CO_{3T} ($mgCO_3/l$)	Co (Organic carbon) (mgC/l)	PO_4	P_3O_{10} (mgP/l)	P_2O_7	pH
Initial	63.0	79.6	19.1	93.5	7.7	149.8	87.4	239.	40.4	8.27	9.40	.73	-
Final	2.1	77.9	17.5	-	-	-	-	7.1	41.4	.41	.07	.003	6.450
	63.1	79.8	19.1	90.0	7.7	148.7	87.5	239.6	40.5	8.29	9.43	.73	-
	2.1	72.1	18.8	-	-	-	-	16.9	39.4	.18	.17	.043	7.5
	63.6	80.3	19.3	92.5	7.7	151.1	87.5	241.3	40.7	8.35	9.5	.73	-
	3.2	59.6	14.8	-	-	-	-	142.0	37.4	.41	.69	.039	8.465
	63.5	139.7	18.9	89.0	7.7	257.0	87.1	236.1	39.9	8.3	9.49	.73	-
	3.8	128.9	20.0	-	-	-	-	7.1	39.3	.038	.198	.008	6.510
	63.7	140.2	18.9	89.3	7.8	257.9	87.2	236.9	40.0	8.32	9.52	.73	-
	2.9	96.5	20.4	-	-	-	-	22.6	41.6	.067	.223	D.L.	7.550
	63.7	140.3	19.0	89.5	7.7	258.0	87.3	237.6	40.1	8.32	9.51	.73	-
	3.2	111.0	17.5	-	-	-	-	144.7	42.7	.124	.249	.086	8.472
	61.7	77.4	18.6	82.0	13.2	146.0	86.3	232.3	39.2	12.6	4.86	.71	-
	2.4	72.1	18.5	-	-	-	-	5.6	37.1	.706	.089	.075	6.430
	68.2	79.2	19.0	83.9	13.5	149.4	86.7	237.8	40.2	12.9	4.98	.73	-
	2.4	72.1	19.3	-	-	-	-	11.3	42.4	.115	.089	.026	7.390
	63.5	79.5	19.1	84.3	13.6	150.0	87.4	238.9	40.3	12.96	5.0	.73	-
	-	-	-	-	-	-	-	155.9	47.7	.995	.121	.073	8.40

TABLE 40

WASTEWATER SAMPLE - INITIAL CONDITIONS

Location	Skyway Treatment Plant Burlington, Ontario		
Phosphate	Ortho-	Poly- (mgP/1)	Pyro-
	2.24	1.93	0.48
Carbon	Organic (mgC/1)	Inorganic ($mgCO_3/1$)	Total (mgC/1)
	42.3	250.5	92.4
Anions	Sulphate	(mg/1)	Chloride
	96.35		106.4
Cations	Sodium	Calcium (mg/1)	Magnesium
	81	83.4	20.0
Initial pH	8.815		

IV.6 EXPERIMENTAL PROCEDURE

The test solutions were prepared from aliquots of standardized stock solutions.* The final volume was made up to 125 or 250 ml (depending upon the nominal flask size) with demineralized and doubly distilled water. The important difference in procedure between those experiments in which one phosphate species precipitated (sections 3 to 5 of Chapter IV) to those in which all three phosphate species precipitated simultaneously was bringing the solutions in equilibrium with the atmosphere. In the former experiments, the flasks were sealed after the addition of dilutant. In the latter cases, the solutions are brought into equilibrium with the atmosphere with an air sparge while the solution pH is being adjusted, (see section 6, Chapter IV). In either case, the stoppered flasks are placed on a vibrating platform shaker situated in a temperature control room (at 25 or 5°C ± .25°C).

While being agitated, the solution pH was monitored with a combination glass electrode (Fisher Scientific Co., Cat. no. 13-639-90) and an Orion Model 801 digital meter. The solution pH can be determined to ± .001 units with this instrument. The solutions were assumed to have reached equilibrium when the solution pH reached a steady state.

The precipitate was removed with a membrane filter. Normally, a membrane with a pore size of 0.45 microns was used. All filters were pre-washed in the manner recommended

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*All stock solutions prepared from reagent grade chemicals.

by "Standard" Methods" (A-1). In those experiments in which a poorly formed precipitate resulted (i.e., a cloudy dispersion), the solution was pretreated by first centrifuging the sample at approximately 3000 rpm for 15 minutes and then passing the centrifugate through a 0.2 micron membrane filter. For those solutions not in contact with the atmosphere, the filtration was carried out in a closed cylinder under a nitrogen atmosphere.

IV.7 ANALYTICAL PROCEDURES

Carbon

Concentrations of organic and inorganic carbon were determined with the Beckman Model 915 Total Organic Carbon Analyzer. In this instrument, carbon species are oxidized to the dioxide in a high temperature catalytic furnace, and the gas concentration then measured with an infrared detector. The total carbon and inorganic carbon concentrations are measured, while the organic portion is determined by difference.

Aqueous samples, twenty microlites in size, were used and the analysis was carried out until the instrument response agreed within one half a scale division after successive injections. The instrument was calibrated daily with at least three fresh standards in the range interest. These standards were made from organic and inorganic stock solutions containing 1000 mg/l C which were less than one week old. The variance estimate associated with this measurement is reported in Table 5.

Calcium, Magnesium and Sodium

The aqueous concentrations of calcium, magnesium, and sodium were determined by adsorption spectroscopy. This method measures the total metal concentration. A Perkin Elmer Model 303 spectrophotometer was used.

The operating procedure is detailed in the manufacturer's manual "Standard Conditions" (P-1). The salient points of interest for each metal are summarized in Table 41. For each metal, the analysis was carried out within a concentration range where the instrument responded linearly. Samples outside this range were detailed with demineralized distilled water. The instrument response to this dilutant was taken as zero concentration of metal. In the analysis of calcium, one drop of a saturated KCl solution was added to each 10 ml of sample to suppress inference from ionization.

The instrument was calibrated before and after each batch of samples were analyzed. If a drift in calibration was observed, a correction to the measured response was made. For each metal, the calibration was carried out with five standards lying in the working concentration range. These standards were prepared from stock solutions containing 1000 mg/l of metal.

The instrument was equipped with a digital readout device which reported the average of the instrument response over eight successive periods. The average of three readings from this monitor was then compared to the calibration curve. The variance estimates for these analyses are:

(i) calcium-----6.8%

(ii) magnesium---3.4%

(iii) sodium------3.0%

TABLE 41

OPERATING CONDITIONS FOR ATOMIC ABSORPTION SPECTROSCOPY

Metal	Concentration Range (mg/l metal)	Flame	Wavelength of Analysis (angstroms)	Addition of Alkalai Salt 1 drop/10ml sample
Calcium	0-10	acetylene-nitrous oxide	4227A	yes
Magnesium	0-5	acetylene-nitrous oxide	2852A	none
Sodium	100-400	air propane	3303A	yes

Chloride

The chloride ion concentration in solution was determined by a potentiometric titration with a selective ion ~~electrode (Orion electrode no. 94~~-17) and the titrant silver nitrate. The procedure is detailed in the manufacturer's brochure, (O-2). The equivalence point in this titration was determined from a Gran plot of the millivolt reading.

Sulphate

The aqueous concentration of sulphate was determined gravimetrically by precipitation with barium chloride. The analytical procedure described in "Standard Methods" (A-1) was followed.

Lanthanum

The total concentration of lanthanum in solution was determined by flame emission spectroscopy. A Jarrell-Ash Model 82-800 spectrophotometer was used. The pertinant operating conditions are:

(i) reducing flame-acetylene-nitrous oxide,
(ii) wavelength--4420A
(iii) slit width-- 75 um
(iv) sample pretreatment--1 drop of saturated KCl solution for every 10 ml of sample,
(v) burner--premix laminar flow with a 5 cm slot.

with the instrument set at a sensitivity of 6, a working concentration of 1 to 50 ppm La was obtained. Samples with concentrations below this were concentrated and those above were diluted. The lower limit of detection was observed to be 0.1 mg/l La.

A calibration curve was prepared from standards at 2, 5, 10, 20, 30, and 50 mg/l La. The instrument response was measured with a 10 millivolt strip chart recorder (Sargent Model S.R.L.). The variance estimated for these analyses is reported in Table 5.

Phosphorus

The following three phosphorus analyses were carried out:

(i) orthophosphate--to measure the concentration of dissolved orthophosphates,

(ii) total phosphates--to measure the total concentration of dissolved ortho- and acid hydrolyzable condensed phosphates (i.e., pyro- and tripoly- species),

(iii) differential analysis--to measure the distribution of soluble ortho-, pyro-, and tripolyphosphate species.

All these analyses were based upon the same colormetric methodology of reacting the orthophosphate ion with ammonium molybdenum in an acid environment as illustrated below:

$$PO_4^{3-} + 12\,(NH_4)_2\,MoO_4 + 24H^+ \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4^+ + 12H_2O. \qquad \text{(IV-1)}$$

The molybdenum in the phosphomolybdate complex is reduced to form a blue sol by the agent aminonaptholsulfonic acid (ANSA). The transmittance of light at 6600A through this sol is proportional to the amount of orthophosphate present.

This colorimetric method (i.e., ANSA method) was carried out on a Technicon Autoanalyzer in an automated fashion. The construction of the continuous flow system, the reagent concentrations and the operational procedure for the first two analyses are reported by the manufacturer (T-2) and Heinke (H-2, H-3). The procedure suggested by the manufacturer was followed with the following exceptions. A dilute acid wask was substituted after each set of four samples in the sampling tray as suggested by Heinke. Second, the bath temperature in the orthophosphate system was reduced from 70 to 35°C to prevent the partial hydrolysis of condensed phosphates (C-4). Third, a double coil (i.e., 40ft.) was substituted for the single coil in the acid hydrolysis reactor to insure complete conversion of the pyro- and tripolyphosphate species (C-4). Figure 29 illustrates schematically the chromatographic separation technique phosphate species connected in series to the total phosphate flow system. The flow system for the orthophosphate analyses is similar to the total phosphate system, except that the hydrolysis step has been removed.

Filtered solutions containing phosphates in the concentration ranges of either 1 to 40 mg/l PO_4 or 0.1 to 10 mg/l

PO_4 were analyzed directly. The increased sensitivity is obtained by increasing the cell length in the spectrophotometer from 15 to 50 mm. Since the techniques of measuring ortho- and total phosphates are quite similar, the measurements were assumed to have the same variance. A pooled estimate which combines measurements from both analyses is reported in Table 5.

Heinke (H-2) had modified the ion-exchange chromatographic analysis specifically for analyzing lake and wastewater samples containing low phosphate concentrations. His procedure was followed with slight modifications. As sources of this information are not widely published, it is reported here.

In addition to the reagent required by the ANSA methodology (T-2), the following solutions are required for the differential analysis:

(i) Stock Buffer Solution: Dissolve 78.5 gm potassium acetate in 800 ml distilled water and adjust to pH 5 with glacial acetic acid. Dilute to 1 litre with distilled water.

(ii) Buffered KCl Solution (1.0M): Add 25 ml of stock buffer solution to 75 gm KCl. Dilute dissolved mixture to 1 litre.

(iii) Buffered KCl Solution (0.2M): Add 50 ml of stock buffer solution to 400 ml of 1 M KCl solution and dilute to 2 litres with distilled water.

(iv) Buffered KCl Solution (1.5M): Add 25 ml of stock buffer solution to 112.5 gm KCl and dilute the dissolved mixture to 1 litre.

(v) HCl Solution: Dilute 10 ml of conc. HCl to 1 litre.

The anion exchange resin used here was AG1-X10 (Bro-Rad Laboratories N.Y.) in the chloride form and with a bead size between 100 to 200 mesh. The column was constructed from a 30 cm length of 1.1 cm (I.D.) glass tubing. The resin bed height was 14 cm.

Before introducing the sample, the column is recharged by pumping through HCl solution for five minutes followed by the 0.2 M KCl solution for fifteen minutes. A sample containing approximately 60 ug of phosphorus is pumped through the column followed by distilled water until all of the sample is on the resin. The 0.2 M KCl solution is next passed through for fifteen minutes in order to provide a better separation of phosphate species. The gradient elution is begun by adding 1.5 M KCl solution to the reagent flask (Note, the volume of 0.2 M KCl solution in the reagent flask is 200 ml when the gradient is started). The quantities of ortho-, pyro-, tripolyphosphate eluted from the column (in that order) are represented by guassian shaped curves displayed on the spectrophotometer's recorder. The fraction of each species present is represented by the ratio of the area under each curve to the total area. In the analyses, the areas were determined by a numerical integration of the curves with Simpson's Rule. The total analysis takes approximately 1½ hours.

Heinke (H-3) tested the reliability of this analysis in determining the fractions of each phosphate species present in wastewater. From his observations, a uniform standard deviation of ± 0.02 was assumed to apply to each fraction. Because the concentration of each species is given by the expression:

$$C_i = X_i P_T \qquad \text{(IV-2)}$$

where C_i is the concentration of phosphate species "i",

X_i is the fraction of species "i" present (determined by the differential analysis)

P_T is the total concentration of phosphorus (determined separately by total phosphate analyses).

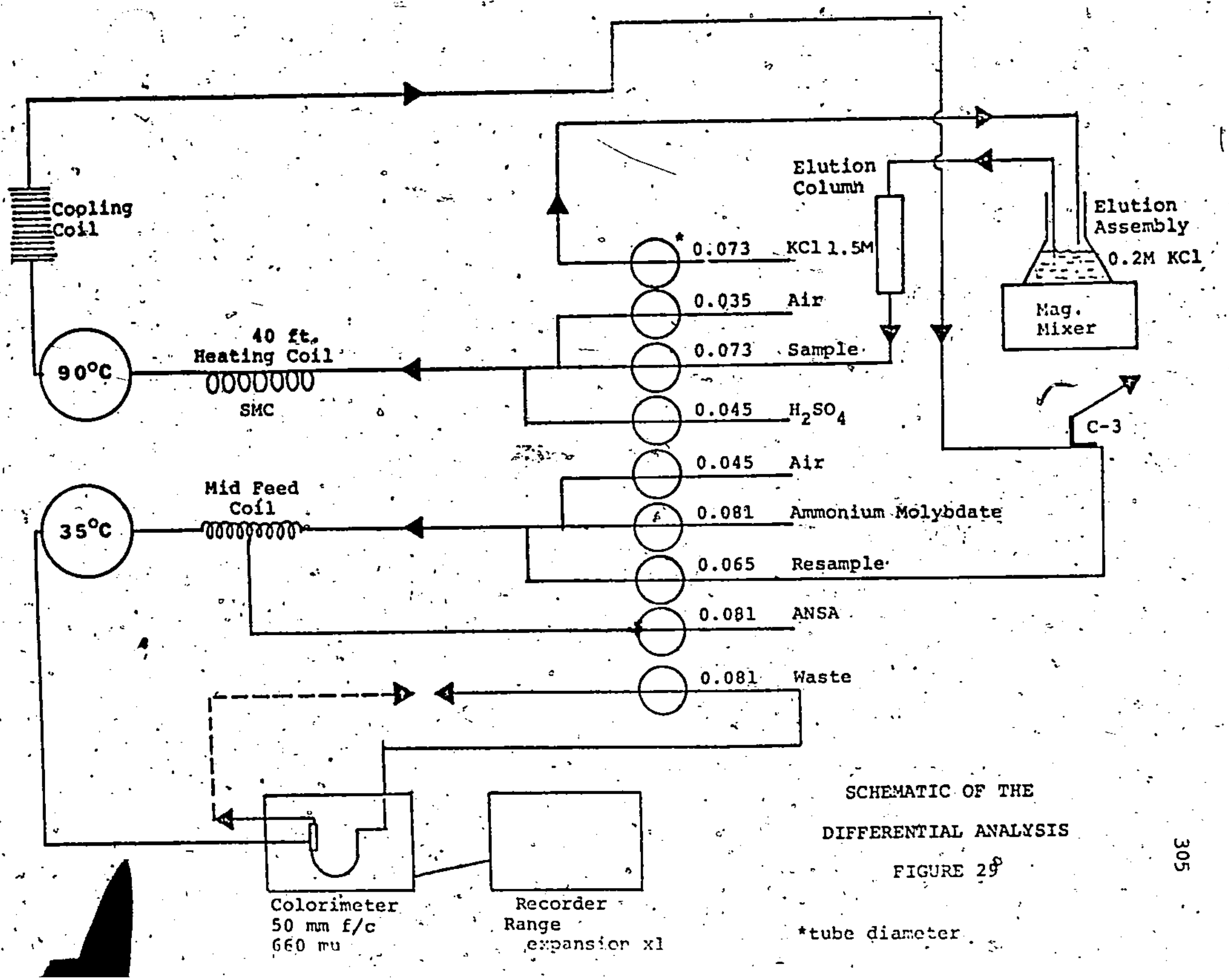
Then an estimate of the error is obtained from its derivative:

$$dC_i = dP_T X_i + dX_i P_T$$

If the size of the derivatives is approximated by the variance in the respective parameters, an estimate of the variance in the concentration of each species is given by:

$$\sigma_{C_i}^2 = \sigma_{P_T}^2 X_i^2 + \sigma_{X_i}^2 P_T^2 \qquad \text{(IV-3)}$$

where σ_{C_i}, σ_{P_T}, and σ_{X_i} are the standard error estimates in species concentration, total concentration, and species fraction respectively. The error estimate for σ_{P_T} is obtained from the relationship reported in Table 5.



SCHEMATIC OF THE

DIFFERENTIAL ANALYSIS

FIGURE 29

*tube diameter

APPENDIX V: COMPUTER MODELS - INPUT DATA

V.1 EQUILIBRIUM MODEL - DISTILLED WATER

TABLE 42

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*****************************************************************************************

               MATRIX OF SPECIES, COMPONENTS, AND REACTIONS


          (FREE ENERGY CONSTANTS EVALUATED AT  5 DEGREES CENTIGRADE)


 SPECIES  FREE ENERGY        STOICHIOMETRIC COEFFICIENTS

          CONSTANTS          AND COMPONENTS
*****************************************************************************************


AQUEOUS SOLUTION (COMPARTMENT - LIQUID)


   H2O    -40.2571     1.0  H+     1.0   OH-
   H+                  1.0  H+
   K+                  1.0  K+
   NA+                 1.0  NA+
   OH-                 1.0  OH-
   CL-                 1.   CL-
   LA+3                1.0  LA+3
   LAOH   -12.2327     1.0  LA+3   1.0   OH-
   LAPOL  -30.28       1.   LA+3   1.    POLY
   LAHPOL-48.81        1.   H+     1.    POLY   1.   LA+3
   POLY                1.   POLY
   HPOLY  -25.2903     1.   H+     1.    POLY
   H2POLY-44.2715      1.   POLY   2.    H+
   H3POLY-53.5818      3.   H+     1.    POLY
```

```
NAPOLY-10.4616   1.   NA+    1.   POLY
KPOLY -10.4616   1.   K+     1.   POLY
PO4-3            1.0  PO4-3
HPO4  -32.3939   1.0  H+     1.0  PO4-3
H2PO4 -52.9824   2.0  H+     1.0  PO4-3
CO3-2            1.0  CO3-2
HCO3- -27.7979   1.0  H+     1.0  CO3-2
H2CO3 -46.4382   2.0  H+     1.0  CO3-2
NACO3--6.9387    1.0  NA+    1.0  CO3-2
NAHCO3-31.2367   1.0  NA+    1.0  H+     1.0  CO3-2
LAPYR -28.42     1.   LA+3   1.   PYRO
H3PYRO-55.2372   1.   PYRO   3.   H+
H2PYRO-45.1448   1.   PYRO   2.   H+
HPYRO -25.6809   1.   PYRO   1.   H+
KPYRO -9.3095    1.   LA+3   1.   PYRO
NAPYRO-9.3095    1.   NA+    1.   PYRO
PYRO             1.   PYRO


ORTHOPHOSPHATE PRECIPITATE (COMPARTMENT - PHOSPHATE)

  LAPO4 -47.05     1.   LA+3   1.   PO4-3      (IF PH LESS THAN 7)
  LAPO4 -42.77     1.   LA+3   1.   PO4-3      (IF SOLUTION IS BASIC)


LANTHANUM CARBONATE PRECIPITATE (COMPARTMENT - CARBONATE)

  LACO3 -77.48     2.   LA+3   3.   CO3-2
```

```
LANTHANUM HYDROXIDE PRECIPITATE (COMPARTMENT - HYDROXIDE)

    LAOH3 -65.32        1.    LA+3   3.    OH-

LANTHANUM TRIPOLYPHOSPHATE PRECIPITATE (COMPARTMENT - POLY - P)

    LAPOLY-170.3        5.    LA+3   2.76 POLY

LANTHANUM PYROPHOSPHATE PRECIPITATE (COMPARTMENT - PYRO - P)

    LAPYRO -153.9       4.    LA+3   3.    PYRO

GAS PHASE (COMPARTMENT - ATMOSPHERE)

    CO2    -61.8778     1.    CO3-2  2.    H+

**************************************************************************************
```

TABLE 43

PARAMETER COVARIANCE MATRIX "COVAR (β)"
(DISTILLED WATER MODEL)

Free Energy Parameter							
$LaPO_4(s)$*	$La_2CO_3(s)$	$La(OH)_3(s)$	$LaP_3O_{10}^{-2}$	$LaHP_3O_{10}$	$La(P_3O_{10})_3(s)$	$LaP_2O_7^-$	$La_4(P_2O_7)_3(s)$
3.022×10^{-3}	6.039×10^{-3}	3.688×10^{-3}	0 ↓	0 ↓	0 ↓	0 ↓	0 ↓
6.039×10^{-3}	1.368×10^{-3}	7.676×10^{-3}					
3.688×10^{-3}	7.676×10^{-3}	5.454×10^{-3}					
0 ↓	0 ↓	0 ↓	5.227×10^{-2}	1.265×10^{-2}	3.821×10^{-2}		
			1.265×10^{-2}	1.012×10^{-1}	2.730×10^{-1}		
			3.821×10^{-2}	2.730×10^{-1}	7.467×10^{-1}		
			0 ↓	0 ↓	0 ↓	2.016×10^{-2}	5.665×10^{-2}
						5.665×10^{-2}	2.545×10^{-2}

*For solutions with pH < 7 replace element β_{11} with 2.396×10^{-2} and set elements β_{12}, β_{21}, β_{13} and β_{31} to zero.

TABLE 44

COMPONENT COVARIANCE MATRIX "COVAR (χu)"

(Distilled Water Model)

	Component			
Lanthanum	Tripolyphosphate	Orthophosphate	Carbonate	Pyrophosphate
1.85×10^{-10}	0.0	0.0	0.0 ↓	0.0 ↓
0 ↓	4.0×10^{-14}			
	0 ↓	4.173×10^{-13}		
		0 ↓	1.1×10^{-11}	
			0	1.024×10^{-13}

uhit (moles/litre

V.2 EQUILIBRIUM MODEL - WASTEWATER

TABLE 45

```
*****************************************************************************

                 MATRIX OF SPECIES, COMPONENTS, AND REACTIONS

          (FREE ENERGY CONSTANTS EVALUATED AT 25 DEGREES CENTIGRADE)

 SPECIES  FREE ENERGY     STOICHIOMETRIC COEFFICIENTS
           CONSTANTS      AND COMPONENTS
*****************************************************************************

AQUEOUS SOLUTION (COMPARTMENT - LIQUID)

     H2O    -40.2571     1.0   H+     1.0   OH-
     H+                  1.0   H+
     K+                  1.0   K+
     NA+                 1.0   NA+
     OH-                 1.0   OH-
     CL-                 1.    CL-
     LA+3                1.0   LA+3
     LAOH   -12.2327     1.0   LA+3   1.0   OH-
     LAPOL  -30.28        1.   LA+3   1.    POLY
     LAHPOL-48.81         1.   H+     1.    POLY   1.   LA+3
     POLY                 1.   POLY
     HPOLY  -25.2903      1.   H+     1.    POLY
     H2POLY-44.2715       1.   POLY   2.    H+
     H3POLY-53.5818       3.   H+     1.    POLY
     NAPOLY-10.4616       1.   NA+    1.    POLY
```

```
KPOLY -10.4616      1.    K+      1.    POLY
PO4-3               1.0   PO4-3
HPO4   -32.3939     1.0   H+      1.0   PO4-3
H2PO4 -52.9824      2.0   H+      1.0   PO4-3
CO3-2               1.0   CO3-2
HCO3-  -27.7979     1.0   H+      1.0   CO3-2
H2CO3 -46.4382      2.0   H+      1.0   CO3-2
NACO3--6.9387       1.0   NA+     1.0   CO3-2
NAHCO3-31.2367      1.0   NA+     1.0   H+      1.0   CO3-2
LAPYR  -28.42       1.    LA+3    1.    PYRO
H3PYRO-55.2372      1.    PYRO    3.    H+
H2PYRO-45.1448      1.    PYRO    2.    H+
HPYRO  -25.6909     1.    PYRO    1.    H+
KPYRO  -9.3095      1.    LA+3    1.    PYRO
NAPYRO-9.3095       1.    NA+     1.    PYRO
PYRO                1.    PYRO
CA+2   0.0          1.    CA+2
CAH2P  -60.2394     1.    CA+2    2.    H+      1.    PO4-3
CAHP   -42.7146     1.    CA+2    1.    H+      1.    PO4-3
CAP    -18.8947     1.    CA+2    1.    PO4-3
CACO3  -11.3828     1.    CA+2    1.    CO3-2
CAHCO3-34.7136      1.    CA+2    1.    H+      1.    CO3-2
CASO4  -9.25076     1.    CA+2    1.    SO4-2
CAOH   -6.6386      1.    CA+2    1.    OH-
CAPOL  -22.6645     1.    CA+2    1.    POLY
CAPYR  -19.6711     1.    CA+2    1.    PYRO
CABPOL-31.9739      1.    CA+2    1.    OH-     1.    POLY
CABPYR-28.5201      1.    CA+2    1.    OH-     1.    PYRO
MG+2   0.0          1.    MG+2
```

```
MGHP   -43.1010     1.    MG+2   1.    H+      1.    PO4-3
MGCO3  -11.8433     1.    MG+2   1.    CO3-2
MGHCO3-34.4834      1.    MG+2   1.    CO3-2   1.    H+
MGSO4  -9.1204      1.    MG+2   1.    SO4-2
MGOH   -9.9667      1.    MG+2   1.    OH-
MGPOL  -23.8158     1.    MG+2   1.    POLY
MGPYR  -20.5922     1.    MG+2   1.    PYRO
MGBPOL-33.3555      1.    MG+2   1.    OH-     1.    POLY
MGBPYR-29.4411      1.    MG+2   1.    OH-     1.    PYRO
LASO4  -12.3489     1.    LA+3   1.    SO4-2
SO4-2  0.0          1.    SO4-2
```

ORTHOPHOSPHATE PRECIPITATE (COMPARTMENT - PHOSPHATE)

```
LAPO4  -47.05       1.    LA+3   1.    PO4-3          (IF PH LESS THAN 7)
LAPO4  -42.77       1.    LA+3   1.    PO4-3          (IF SOLUTION IS BASIC)
```

LANTHANUM CARBONATE PRECIPITATE (COMPARTMENT - CARBONATE)

```
LACO3  -77.48       2.    LA+3   3.    CO3-2
```

LANTHANUM HYDROXIDE PRECIPITATE (COMPARTMENT - HYDROXIDE)

```
LAOH3  -65.32       1.    LA+3   3.    OH-
```

LANTHANUM TRIPOLYPHOSPHATE PRECIPITATE (COMPARTMENT - POLY - P)

```
LAPOLY-170.3        5.    LA+3   2.76 POLY
```

```
LANTHANUM PYROPHOSPHATE PRECIPITATE (COMPARTMENT - PYRO - P)


    LAPYRO -153.9      4.     LA+3    3.    PYRO
 CALCIUM HYDROXYAPATITE (COMPARTMENT - APATITE)

    HAP    -146.64     5.     CA+2    3.    PO4-3  1.   OH-
 CALCIUM MAGNESIUM CARBONATE (COMPARTMENT - CA - MG-CO3)

    CACO3*-25.76       1.     CA+2    1.    CO3-2


 GAS PHASE (COMPARTMENT - ATMOSPHERE)


    CO2    -61.8778    1.     CO3-2   2.    H+


*******************************************************************************************
```

TABLE 46

PARAMETER COVARIANCE MATRIX "COVAR (β)"
(WASTEWATER MODEL)

No.	Species	Variance Estimate				
1	$LaPO_4(s)$*	$\beta_{1,1}=3.022x10^{-3}$	$\beta_{12}=6.039x10^{-3}$	$\beta_{13}=3.688x10^{-3}$	$\beta_{1,4}$ to $\beta_{1,16}=0$	
2	$La_2(CO_3)_3(s)$	$\beta_{1,2}=6.039x10^{-3}$	$\beta_{22}=1.368x10^{-3}$	$\beta_{2,3}=7.676x10^{-3}$	$\beta_{2,4}$ to $\beta_{1,16}=0$	
3	$La(OH)_3(s)$	$\beta_{3,1}=3.688x10^{-3}$	$\beta_{3,2}=7.676x10^{-3}$	$\beta_{3,3}=5.454x10^{-3}$	$\beta_{3,4}$ to $\beta_{1,16}=0$	
4	$LaP_3O_{10}^{-2}$	$\beta_{4,1}$ to $\beta_{4,3}=0$	$\beta_{4,4}=5.227x10^{-3}$	$\beta_{4,5}=1.265x10^{-2}$	$\beta_{4,6}=3.821x10^{-2}$	$\beta_{4,7}$ to $\beta_{4,16}=0$
5	$LaHP_3O_{10}^{-}$	$\beta_{5,1}$ to $\beta_{5,3}=0$	$\beta_{5,4}=1.265x10^{-2}$	$\beta_{5,5}=1.021x10^{-1}$	$\beta_{5,6}=2.730x10^{-1}$	$\beta_{5,7}$ to $\beta_{5,16}=0$
6	$La_5(P_3O_{10})_3(s)$	$\beta_{6,1}$ to $\beta_{6,3}=0$	$\beta_{6,4}=3.821x10^{-2}$	$\beta_{6,5}=2.730x10^{-1}$	$\beta_{6,6}=7.467x10^{-1}$	$\beta_{6,7}$ to $\beta_{6,16}=0$
7	$LaP_2O_7^{-}$	$\beta_{7,1}$ to $\beta_{7,6}=0$	$\beta_{7,7}=2.016x10^{-2}$	$\beta_{7,8}=5,665x10^{-2}$	$\beta_{8,8}$ to $\beta_{8,16}=0$	
8	$La_4(P_2O_7)_3$	$\beta_{8,1}$ to $\beta_{8,6}=0$	$\beta_{8,7}=5.665x10^{-2}$	$\beta_{8,8}=2.545x10^{-2}$	$\beta_{9,9}$ to $\beta_{9,16}=0$	
9	$CaP_3O_{10}^{-3}$	$\beta_{9,1}$ to $\beta_{8,8}=0$	$\beta_{9,9}=4.771x10^{-1}$	$\beta_{9,10}$ to $\beta_{9,16}=0$		
10	$CaOHP_3O_{10}^{-4}$	$\beta_{10,11}$ to $\beta_{10,9}=0$	$\beta_{10,10}=1.325$	$\beta_{10,11}$ to $\beta_{10,16}=0$		
11	$CaP_2O_7^{-2}$	$\beta_{11,1}$ to $\beta_{11,10}=0$	$\beta_{11,11}=.4771$	$\beta_{11,12}$ to $\beta_{11,16}=0$		
12	$CaOHP_2O_7^{-3}$	$\beta_{12,1}$ to $\beta_{12,11}=0$	$\beta_{12,12}=1.325$	$\beta_{12,13}$ to $\beta_{12,16}=0$		
13	$MgP_3O_{10}^{-3}$	$\beta_{13,1}$ to $\beta_{13,12}=0$	$\beta_{13,13}=.4771$	$\beta_{13,14}$ to $\beta_{13,16}=0$		
14	$MgOHP_3O_{10}^{-4}$	$\beta_{14,1}$ to $\beta_{14,13}=0$	$\beta_{14,14}=1.325$	$\beta_{14,15}$ to $\beta_{14,16}=0$		
15	$MgP_2O_7^{-2}$	$\beta_{15,1}$ to $\beta_{15,14}=0$	$\beta_{15,15}=.4771$	$\beta_{16}=0$		
16	$MgOHP_2O_7^{-3}$	$\beta_{16,1}$ to $\beta_{16,15}=0$	$\beta_{16,16}=1.325$			

*For solutions with pH < 7 replace element β_{11} with $2.396x10^{-2}$ and set elements β_{12}, β_{21}, β_{13} and β_{31} to zero.

TABLE 47

COMPONENT COVARIANCE MATRIX "COVAR (xu)"

(Wastewater Model)

		Component					
anthanum	Tripolyphosphate	Pyrophosphate	Orthophosphate	Sulphate	Calcium	Magnesium	Carbonate
$9x10^{-11}$	0	0	0	0	0	0	0
0	$4x10^{-12}$	↓	↓	↓	↓	↓	↓
↓	0	$4x10^{-12}$					
	↓	0	$4x10^{-12}$				
		↓	0	$16x10^{-10}$			
			↓	0	$3.03x10^{-9}$		
				↓	0	$4.2x10^{-10}$	
					↓	0	$2.41x10^{-9}$

nits (moles/Liter

APPENDIX VI: LISTING OF COMPUTER MODELS

VI.1 PARAMETER ESTIMATION

The computer subroutines which are used in the parameter estimation problem and listed here are:

(i) TST (Main Program)
(ii) SIMPLEX
(iii) OBJECT
(iv) MODEL.

In addition to the "CHEMIST" subroutines, the following utility subroutines are used. These are:

(i) MINSVE (Matrix Inversion)
(ii) OUTPLT (Plotting Program)
(iii) PLOTPT (Plotting Program).

This latter group of computer programs are available on permanent file at the McMaster Computer Centre.

```
C      PARAMETER ESTIMATION PROGRAM - MAIN PROGRAM
       PROGRAM TST(INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT)
       REAL    KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS
       COMMON AIJ(460), IROW(460), JCOL(460)                             NZSC0100
       REAL AIJ,NAME,MWW                                                 NZSC0110
       COMMON /HOL8/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK, NZSC0130
                                                                         NZSC0140
     1    H2O,HPLUS                                                      NZSC0160
       COMMON /REAL8/ BBB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,    NZSC0170
     1    XSTART,BARMIN,SLACKS,ALITER,KT,B(60),PIE(75),V1(75),V2(75),    NZSC0180
     2    V3(75),V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170),  NZSC0190
     3    XBAR(25),R(75,75),FE,FE2,ERMB,XEMB,ERMA,XEMA
       COMMON /INTGR/ NAMEND,NCOMP,N,NIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,NZSC0210
                                                                         NZSC0220
     1    KE,MAXM,MAXP,MAXN,MAXND,NCYCLE,NBSTAR,KPF,                     NZSC0280
     2    NAIJ,MAXAIJ,IOPT,MTOG,MARITH,KL(26),JCOMP(170),NEMB,NEMA       NZSC0240
       EQUIVALENCE (N,NTOT)                                              NZSC0250
       INTEGER PF                                                        NZSC0270
       COMMON /TOGL/ IARITH,IFIND,INTLTE,INSOLV,IJOHN,ILP,IMATRX,IPUSH,
     1                  IROWS,ISCALE                                     NZSC0290
       COMMON/MOLER/CMW(60),Z1(60),DENSP,DENS,MWW,SMW(170),Z(170),
      1TOT,ISTOP,K,JI,JT,A1,A2,AC(170)
C THE PO4, CO3, AND OH SOL. PROD. ARE BEING DETERMINED
       COMMON /JET/ EP(30),EL(30),ER(3,30),ECA(20),AB(30)
       COMMON /MOD/ STOR(30,30),EC(15,30),PR(7,30),PD(7,10),PDI(7,10),
      1CPRINT,XTVX(3,3)
       DIMENSION SP(30,31),RMS(3),RESID(3,30),N1(12),WORK(3),VAR(2,2)
C NX NO. OF EXPERIEMNTS
C NMR NO. OF MODEL RESPONES
C MNIV NO. OF INDEPENDENT VARIABLES
C NP NO. OF PARAMETERS
       NX=9  $  NMR=2  $  MNIV=4  $  NP=3
C SUBROUTINES CALLED FORM THE RAND SOFTWARE PACKAGE ARE IDENTIFIED BY THE LABEL
  CHEMIST IN COLS. 73-79                                                 CHEMIST
       CALL START                                                        CHEMIST
       CALL INPUT
C CMW COMPONENT MOLECULAR WEIGHTS
C Z1 CHARGE ON COMPONENT ATOMS OR MOLECULAR GROUPS
       READ(5,100) (CMW(I), I = 1,M)
       READ(5,100) (Z1(I), I = 1,M)
       READ(5,100) DENSP,MWW,A1,A2
       CALL PAGE
       CALL SECOND(TIME)
       WRITE(6,220) TIME
       CALL MWCALC(6HLIQUID,1.,MWC)
C   READ IN INITIAL CONDITIONS
C EP, EL, AND E3A ARE NO. OF MOLES OF PHOSPHATE, LANTHANUM AND CARBONATE
C  INITIALLY PRESENT
C ER EXPERIMENTAL OBSERVATIONS
C AB MOLES OF ACID OR BASE INITALLY ADDED TO THE SYSTEM
       DO 1 I = 1,NX
```

```
 1    READ(5,100) EP(I),EL(I),ECA(I),ER(1,I),ER(2,I),ER(3,I),AB(I)
C READ IN  INITIAL ESTIMATES
C SP INITIAL ESTIMATES FOR THE SIMPLEX SEARCH
      READ(5,100) ((SP(I,J), J=1,4), I=1,3)
      DO 2 I = 1,NX
      DO 2 J = 1,N
C STOR ESTIMATES OF THE SPECIES MOLE NUMBERS FROM THE PREVIOUS ITERATION FOR
C  FOR EACH EXPERIMENT
 2    STOR(J,I) = XSTART
C CALL SIMPLEX
      CPRINT = 0.
      CALL PAGE
      CALL SIMPLEX(3,SP,1.E-03,50,1.,.5,2.,2)
C PLOTBACK OF THE FINAL RESULTS
      CPRINT = 1.
      C(17) = SP(1,1)
      C(18) = SP(2,1)
      C(19) = SP(3,1)
      RMS(1) = 0.
      RMS(2) = 0.
      PF = 0
      CALL SECOND(TIME)
      WRITE(6,220) TIME
      DO 3 I = 1,NX
      EC(1,I) = E3A(I) + 2.*EP(I)
      EC(2,I) = ECA(I)
      EC(3,I) = EP(I)
      EC(4,I) = EL(I)
      EC(5,I) = 0.
      EC(6,I) = ECA(I)
      EC(7,I) = EP(I)
      EC(8,I) = EL(I)*3.
      EC(9,I) = AB(I)
C SUBROUTINE MODEL DIRECTS THE CHEMIST SUBROUTINES TO CALCULATE THE
C  EQUILIBRIUM COMPOSITION AND PARTIAL DERIVATIVES
C NE EXPERIMENT NUMBER
      CALL MODEL(I)
      WRITE(6,210)
      WRITE(6,208) KN(17),KN(18),KN(19)
      WRITE(6,209) X(17),X(18),X(19)
      RESID(1,I) = (ER(1,I)-PR(1,I))/ER(1,I)
      RESID(2,I) = (ER(2,I)-PR(2,I))/ER(2,I)
      RMS(1) = RMS(1) + RESID(1,I)**2
      RMS(2) = RMS(2) + RESID(2,I)**2
 3    CONTINUE
      CALL PAGE
      WRITE(6,200)
      DO 7 I = 1,NX
      EP(I) = EP(I)*1000.*CMW(7)
      ECA(I) = ECA(I)*1000.*CMW(6)
      EL(I) = EL(I)*1000.*CMW(4)
      WRITE(6,201) ER(1,I),ER(2,I),ER(3,I),EP(I),ECA(I),EL(I)
      WRITE(6,202) PR(1,I),PR(2,I),PR(4,I)
 7    CONTINUE
      DF = FLOAT(NX*NMR-NP)
      RMS(1) = SQRT(RMS(1)/DF)
      RMS(2) = SQRT(RMS(2)/DF)
```

```
      WRITE(6,203) RMS(1),RMS(2)
C PLOT OF THE RESIDUALS VS Y PREDICTED
      DO 8 I = 1,NX
      CALL PLOTPT(PR(1,I),RESID(1,I),4)
 8    CONTINUE
      CALL OUTPLT
      WRITE(6,205)
 205  FORMAT(5X,*RESIDUAL VS Y-PREDICTED   PHOSPHATE*)
      DO 9 I = 1,NX
      CALL PLOTPT(PR(2,I),RESID(2,I),4)
 9    CONTINUE
      CALL OUTPLT
      WRITE(6,206)
 206  FORMAT(5X,*RESIDUAL VS Y-PREDICTED  CARBONATE*)
      STOP
 100  FORMAT(8F10.3)
 200  FORMAT(///20X,*PLOTBACK OF THE MODEL FOR THE LA - CO3 - PO4 SYSTEM
     1*,/21X,*RESPONSE*,32X,*INITIAL CONDITIONS*,//12X,*PHOSPHATE     CA
     2RBONATE          PH         PHOSPHATE     CARBONATE      LANTHANUM*,//
     330X,* - MG/L - *)
 201  FORMAT(//2X,*MEASURED  *,2(3X,1PE10.3),6X,0PF6.3,1X,3(3X,1PE10.3))
 202  FORMAT(/2X,*PREDICTED *,2(3X,1PE10.3),6X,0PF6.3)
 203  FORMAT(///10X,*ROOT MEAN SQUARE - PHOSPHATE .*,1PE10.3,*  -  CAR
     1BONATE  *,E10.3)
 208  FORMAT(//10X,4(A6,6X))
 209  FORMAT(/10X,4(1PE10.3,2X))
 210  FORMAT(///10X,*SOLID PHASE DISTRIBUTION*)
 220  FORMAT(//10X,*TIME ELAPSED  *,1PE10.3,*  SECONDS*)
      END
      SUBROUTINE MODEL(NF)
      REAL    KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS                       NZSC0100
      COMMON AIJ(460), IROW(460), JCOL(460)                             NZSC0110
      REAL AIJ,NAME,MWW                                                 NZSC0130
      COMMON /HCLB/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK, NZSC0140
     1    H2O,HPLUS
      COMMON /REAL8/ BBR(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,    NZSC0170
     1    XSTART=BARMIN,SLACKS,ALITER,RI,B(60),PIE(75),V1(75),V2(75),   NZSC0180
     2    V3(75),V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170), NZSC0190
     3    XBAR(25),R(75,75),FE,FE2,ERMB,XEMB,ERMA,XEMA                  NZSC0210
      COMMON /INTGR/ M,MEND,NCOMP,N,NIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,NZSC0220
     1    KE,MAXM,MAXP,MAXN,MAXMD,NCYCLE,NBSTAR,NPF,                    NZSC0230
     2    NRIJ,MAXAIJ,IOPT,NLOG,MARITH,NL(26),JCOMP(170),NEMB,NEMA      NZSC0240
      EQUIVALENCE (N,NIJ)                                               NZSC0250
      INTEGER PF
      COMMON /TOGL/ IARITH,IFIND,INTITL,INSOLV,IJOHN,ILP,IMATRX,IPUSH,  NZSC0270
     1                 IROWS,ISCALE                                     NZSC0290
      COMMON/MOLER/CMW(60),Z1(60),DENSP,DENS,MWX,SMW(170),Z(170),
     1TOT,ISTOP,K,JI,JT,A1,A2,AC(170),ECA(20),AB(30)
      COMMON /JET/ EP(30),EL(30),EK(3,30),PK(7,30),PD(7,10),PDI(7,10),
      COMMON /MOD/ STOR(30,30),EC(15,30),
     1CPRINT,XTVX(3,3)
      DIMENSION ILOOP(5,8),NC(10),NIV(6),AA(20),TNMR(6)
      DATA (TNMR(I), I=1,3) /6H LA+3 ,6H PO4  ,6H CO3  /
C AA NO. MOLES OF ACID
      DATA (AA(I), I=1,10) /10*0./
C NIV COMPONENT NUMBERS
      DATA (NIV(I),  I=1,4) /7,6,4,5/
```

```
C NC FREE ENERGY PARAMETER NUMBERS
      DATA (NC(I), I=1,3) /17,18,19/
C ILOOP DO - LOOP PARAMETERS USED TO CALCULATE THE MODEL RESPONSE AND PARTIAL
C   DERIVATIVES
      DATA ((ILOOP(I,J), J=1,5), I=1,3) /9,10,11,0,0,12,13,14,15,16,7,8,
     A0,0,0/
C NMR NO. OF MODEL RESPONSES
C NP NO. OF PARAMETERS
C MNS MAXIMUM NO OF SPECIES REQUIRED TO FORM A RESPONSE.
C MNIV TOTAL NO OF INDEPENDENT VARIABLES
      NMR=3  $  NP=3  $  MNS=5  $  MNIV=4
      DO 1 I = 1,M
    1 BBB(I,2) = EC(I,NE)
      BMULT(4) = EC(M+1,NE)
      BMULT(5) = AA(NE)                                               CHEMIST
      CALL ROWS(-1)
      PF = -1
      DO 2 J = 1,N
      AC(J) = 1.
    2 X(J) = STOR(J,NE)                                               CHEMIST
      CALL SOLVE
      DO 3 J = 1,N
    3 STOR(J,NE) = X(J)
C DENSITY OF THE SOLUTION
      DENS = 0.
      DO 4 J = JI,JT
    4 DENS = DENS + X(J)*SMW(J)
      DENS = DENS*1.E-03*ALITER/X(1)
      IF(CPRINT.GT.0.) PF = 0
      IF(CPRINT.GT.0.) CALL PAGE
      CALL CORR(6HLIQUID,0.,5)
      CALL MOLAR(6HLIQUID,CPRINT,1)
      IF(CPRINT) 20,20,21
   21 DO 22 J = 1,N
   22 STOR(J,NE) = X(J)
   20 MARITH = 0                                                      CHEMIST
      CALL ARITH
      DO 5 I = 1,NMR
      PR(I,NE) = 0.
      DO 12 J = 1,NP
   12 PD(I,J) = 0.
      DO 13 J =1,MNIV
   13 PDI(I,J) = 0.
    5 CONTINUE
      DO 6 I = 1,NMR
      DO 7 J=1,MNS
      IF(ILOOP(I,J).LE.0) GO TO 7
      PR(I,NE) = PR(I,NE) + XI(ILOOP(I,J))
      DO 9 L=1,MNIV
C BJACOB - CHEMIST FUNCTION PROGRAM
    9 PDI(I,L) = PDI(I,L) + BJACOB(NIV(L),ILOOP(I,J))*XI(ILOOP(I,J))/X(I
     1LOOP(I,J))
      DO 10 L=1,NP
C  CJACOB CHEMIST FUNCTION PROGRAM
   10 PD(I,L) = PD(I,L) + CJACOB(ILOOP(I,J),NC(L))*XI(ILOOP(I,J))/X(ILOO
     1P(I,J))
    7 CONTINUE
```

```
      PR(I,NE) = PR(I,NE)*1000.*CMW(NIV(I))
      DO 11 L = 1,NP
11    PD(I,L) = PD(I,L)*1000.*CMW(NIV(I))
      DO 8 L =1,NNIV
8     PDI(I,L) = PDI(I,L)*1000.*CMW(NIV(I))
6     CONTINUE
C PHCALC CHEMIST FUNCTION PROGRAM
      PR(NNR+1,NE) = PHCALC(N)
      IF(CPRINT.GT.0.) GO TO 14
      RETURN
14    DO 16 I=1,NNR
      WRITE(6,200) TNMR(I),(NN(NC(J)), J=1,NP)
      WRITE(6,201) (PD(I,J), J=1,NP)
      WRITE(6,202) TNMR(I),(NN(NIV(J)), J=1,NNIV)
      WRITE(6,201) (PDI(I,J), J=1,NNIV)
16    CONTINUE
      RETURN
200   FORMAT(/10X,*PARTIAL DERIVATIVES *,A6,*WRT FREE ENERGY VALUES*,/7(
     12X,A6,7X))
201   FORMAT(/7(2X,1PE10.3,3X))
202   FORMAT(/10X,*PARTIAL DERIVATIVES OF RESPONSE *,A6,*WRT INDEPENDENT
     1 VARIABLES*,/7(2X,A6,7X))
      END
C SUBROUTINE TO CALCULATE THE OBJECTIVE FUNCTION FOR THE SIMPLEX SEARCH
      SUBROUTINE OBJECT(Y,DET,NTRY,NMAX)
      COMMON /MOD/ STOR(30,30),EC(15,30),PR(7,30),PD(7,10),PDI(7,10),
     1CPRINT,XTVX(3,3)
      COMMON /SET/ EP(30),EL(30),ER(3,30),ECA(20),AB(30)
      COMMON /REAL8/ BEB(60,5),PH(25),I(20),BMULT(5),TOL1,TOL2,XMIN,    MZSC0160
     1    XSTART,BARMIN,SLACKS,ALITER,NT,B(60),PTS(75),V1(75),V2(75),   MZSC0170
     2    V3(75),V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170), MZSC0180
     3    XBAR(25),R(75,75),FE,FE2,ERMB,XEMB,ERMA,XEMA                  MZSC0190
      DIMENSION Y(3),VAR(2,2),V(2,2)
      DIMENSION SV(6),N1(8),WORK(2)
      DET = 0.
C THIS SECTION DETERMINES IF TIME REMAINS FOR THE SEARCH TO CONTINUE
      CALL SECOND(TIME)
      WRITE(6,200) NTRY,TIME
200   FORMAT(//10X,*OBJECT HAS BEEN CALLED *,I3,* TIMES   RUN TIME  *,1
     1PE10.3,* SECONDS*)
C IF NO TIME LEFT NO OF CYCLES COMPLETED IS SET TO THE MAXIMUM PERMITTED
      IF(TIME.GT.425.) NTRY = NMAX
      DO 1 I = 1,2
      DO 1 J = 1,2
1     V(I,J) = 0.
C NX NO. OF EXPERIMENTS
      NX=9
C TRANSFER OF INFORMATION INTO ARRAYS FOR USE BY THE SUBROUTINE MODEL
      C(17) = Y(1)
      C(18) = Y(2)
      C(19) = Y(3)
      DO 2 I = 1,NX
      EC(1,I) = ECA(I) + 2.*EP(I)
      EC(2,I) = ECA(I)
      EC(3,I) = EP(I)
      EC(4,I) = EL(I)
      EC(5,I) = 0.
```

```
      EC(6,I) = ECA(I)
      EC(7,I) = EP(I)
      EC(8,I) = EL(I)*3.
      EC(9,I) = AB(I)
C CALCULATE THE EQUILIBRIUM COMPOSITION WITH THE PRESENT FREE ENERGY PARAMETER
C    ESTIMATES
      CALL MODEL(I)
C ESTIMATE THE EFFECTIVE ERRORS
      EV(1) = (0.0381*ER(1,I))**2
      EV(2) = (0.0137*ER(2,I))**2
      EV(3)=1.E-12  $  EV(4)=1.E-10  $  EV(5)=1.E-12  $  EV(6)=1.E-10
      DO 3 II = 1,NMR
      DO 3 J=1,NMR
      VAR(II,J) =0.
      DO 4 L=1,NNIV
4     VAR(II,J) = VAR(II,J) + PDI(II,J)*PDI(J,L)*EV(2+L)
      IF(II.EQ.J) VAR(II,J) = VAR(II,J) + EV(II)
3     CONTINUE
      CALL MINVSE(VAR,NMR,NMR,1.E-20,IERR,N1,WORK)
      DO 5 II = 1,2
      DO 5 J=1,2
5     V(II,J) = (ER(II,I)-PR(II,I))*VAR(II,J)*(ER(J,I)-PR(J,I)) + V(II,J
     A)
2     CONTINUE
      DET = V(1,1) + V(2,2) + V(2,1) + V(1,2)
      RETURN
      END
```

```
      SUBROUTINE SIMPLEX(N,X,EPS,NMAX,ALPHA,BETA,GAMA,NWRIT)
      DIMENSION X(30,31),F(30),Y(30),XR(30),XH(30),XU(30),XS(30),XL(30),
     1XE(30),XC(30)
C
C*************************************************************************
C
C  OPTIMIZATION BY THE SIMPLEX METHOD
C
C*************************************************************************
C  NOTATION AND ALGORITHM IS THE SAME AS THAT FOUND IN THE BOOK--
C
C      METHODS FOR UNCONSTRAINED OPTIMIZATION PROBLEMS BY J.KOWALIK AND
C      M.R.OSBORNE ELSEVIER,NY(1968)
C  EXCEPT FOR SLIGHT CHANGES IN NOTATION IT IS THE SAME AS THAT FOUND
C      IN THE PAPER BY NELDER AND MEAD (COMPUTER J.,VOL7,308(1965)
C
C
C
C  NWRIT -  PRINT CONTROL
```

```
C  XH -  THE HIGHEST VERTEX (FUNCTION VALUE =FXH)
C  XS -  THE SECOND HIGHEST VERTEX (FUNCTION VALUE = FXS)
C  XL -  THE LOWEST VERTEX (FUNCTION VALUE = FXL)
C  XO IS THE CENTROID OF ALL X EXCLUDING XH
C  VALUES OF ALPHA, BETA AND GAMA ARE SET IN PARAMETER LIST
C  FOR REFLECTION, CONTRACTION AND EXPANSION RESPECTIVELY
      AL1=ALPHA+1.
      BET1=1.-BETA
      GAM1=1.-GAMA
C  MAXIMUM NUMBER OF FUNCTION EVALUATIONS IS SET
C                 THE PROGRAM STOPS WHEN FOR SOME CONSECUTIVE FUNCTION
C     EVALUATIONS THE FUNCTION VALUES DIFFER BY LESS THAN EPS
C     THIS IS THE BOX CRITERION (REF COMPUTER J.,VOL 8,42(1965))
C  FOR THE BOX CRITERION FUN1 IS SET TO AN INITIALLY VERY HIGH VALUE
C     AFTER THE FIRST ITERATION THE VALUE OF FUN1 IS THE VALUE OF THE
C  FUNCTION AT THE ITERATION BEFORE THE PRESENT ITERATION
C THEN FOR THE BOX CRITERION FSTOP = ABS (FUN-FUN1)
C  NUMBER OF POINTS IN SIMPLEX IS N1=1+N
C
C     EVALUATE INITIAL SIMPLEX
C
C  X(J,I)=X(CO-ORDINATE,POINT)
C  EVALUATE FUNCTION,AT EACH X(J,I)
      WRITE(6,901)
  901 FORMAT (////* OPTIMIZATION USING THE SIMPLEX METHOD *////)
      FUN1=1.E06
      FUN2=1.E6
      NTRY=0
      N1=N+1
      RN=N
 21   DO 2 I = 1,N1
      DO 22 J = 1,N
      Y(J)=X(J,I)
 22   CONTINUE
      NTRY=NTRY+1
      CALL OBJECT(Y,F(I),NTRY,NMAX)
 2    CONTINUE
      IF (NWRIT .LE. 0) GO TO 1001
      WRITE(6,605)
 605  FORMAT(1X,*X VALUES*)
      DO 51 IL=1,N1
      WRITE(6,603)(X(IM,IL),IM=1,N)
 51   CONTINUE
 603  FORMAT(1X,10E12.5)
      WRITE(6,606)
 606  FORMAT(1X,*F VALUES*)
      WRITE(6,603)(F(KK),KK=1,N1)
 1001 CONTINUE
      DO 36 I = 1,N
      XR(I)=0.
      XO(I)=0.
      XE(I)=0.
      XS(I)=0.
      XH(I)=0.
      XC(I)=0.
      XL(I)=0.
 36   CONTINUE
```

```
      GO TO 24
   11 IF(NTRY.GE.NMAX) GO TO 23
   24 FXH = F(1)
      IXH=1
      DO 3 I = 2,N1
      IF(F(I).LT.FXH)GO TO 3
      FXH=F(I)
      IXH=I
3     CONTINUE
      DO 101 I = 1,N1
      IF (I .EQ. IXH) GO TO 101
      FXS = F(I)
      GO TO 102
  101 CONTINUE
  102 CONTINUE
      DO 4 I = 1,N1
      IF(F(I).LT.FXS)GO TO 4
      IF(I.EQ.IXH)GO TO 4
      FXS=F(I)
      IXS=I
4     CONTINUE
      FXL=F(1)
      IXL=1
      DO 5 I = 2,N1
      IF(F(I).GT.FXL)GO TO 5
      FXL=F(I)
      IXL=I
5     CONTINUE
      FSTP=ABS(FUN2-FXL)
      FUN2=FXL
C
C     PRINT ONLY IF THERE IS AN IMPROVEMENT IN MINIMUM VALUE
C
      IF(FSTP.LT.1.E-6) GO TO 777
      IF(NWRIT.LE.1) GO TO 1002
      WRITE(6,610) FSTOP,NTRY
610   FORMAT(1H0,*ERROR  *,E12.5, *   FUN EVAL NO  *,I5)
      WRITE(6,605)
      DO 6010  IL=1,N1
      WRITE(6,603) (X(IM,IL),IM=1,N)
6010  CONTINUE
      WRITE(6,606)
      WRITE(6,603) (F(KK),KK=1,N1)
 1002 CONTINUE
  777 DO 8 I=1,N
      XH(I)=X(I,IXH)
      XS(I)=X(I,IXS)
      XL(I)=X(I,IXL)
8     CONTINUE
C   CALCULATE XO
C   CALCULATE XH,XS,AND XL
      DO 7 J = 1,N
      SUM=0.
      DO 6 I = 1,N1
      IF(I.EQ.IXH)GO TO 6
      SUM=SUM+X(J,I)
6     CONTINUE
```

```
      XO(J)=SUM/RN
7     CONTINUE
      NTRY=NTRY+1
      CALL OBJECT(XO,FXO,NTRY,NMAX)
      FSTOP=0.
      DO 810 I=1,N1
      FSTOP=FSTOP+(F(I)-FXO)**2
  810 CONTINUE
      FSTOP=SQRT(FSTOP/RN)
      IF(NTRY.GE.NMAX)GO TO 23
      IF(FSTOP.LT.EPS) GO TO 23
C REFLECTION
      DO 31 I = 1,N
      XR(I)=AL1*XO(I)-ALPHA*XH(I)
31    CONTINUE
      NTRY=NTRY+1
      CALL OBJECT(XR,FXR,NTRY,NMAX)
      IF(NTRY.GE.NMAX)GO TO 23
      IF((FXS.GE.FXR).AND.(FXR.GE.FXL))GO TO 9
      IF(FXR.LT.FXL)GO TO 12
      IF((FXH.GT.FXR).AND.(FXR.GT.FXS))GO TO 15
C  CONTRACTION
35    DO 33 I = 1,N
      XC(I)=BETA*XH(I)+BET1*XO(I)
33    CONTINUE
      NTRY=NTRY+1
      CALL OBJECT(XC,FXC,NTRY,NMAX)
      IF(NTRY.GE.NMAX)GO TO 23
      IF(FXH.GT.FXC)GO TO 17
C  SHRINKING OF SIMPLEX
      WRITE(6,650)(XL(I),I=1,N)
650   FORMAT(1H0,*SHRINK SIMPLEX,XL =    *,3E12.5)
      DO 20 I = 1,N1
      DO 20 J = 1,N
      IF(I.EQ.IXL) GO TO 800
      X(J,I)=.5*(X(J,I)+XL(J))
  800 CONTINUE
20    CONTINUE
      GO TO 21
C REPLACE XH BY XR AND RESTART PROCESS
9     DO 10 J = 1,N
      X(J,IXH)=XR(J)
      XH(J)=XR(J)
10    CONTINUE
      F(IXH)=FXR
      GO TO 11
C  EXPANSION
12    DO 32 I=1,N
      XE(I)=GAMA*XR(I)+GAM1*XO(I)
32    CONTINUE
      NTRY=NTRY+1
      CALL OBJECT(XE,FXE,NTRY,NMAX)
      IF(FXL.GT.FXE)GO TO 13
C  EXPANSION UNSUCCESSFUL SO GO TO 9 TO REPLACE XH BY XR
      GO TO 9
C  EXPANSION SUCCESSFUL, REPLACE XH BY XE
13    DO 14 J = 1,N
```

```
      X(J,IXH)=XE(J)
      XH(J)=XE(J)
   14 CONTINUE
      F(IXH)=FXE
      GO TO 11
C  REPLACE XH BY XR AND CONTRACT
   15 DO 16 J=1,N
      XH(J)=XR(J)
      X(J,IXH)=XR(J)
   16 CONTINUE
      F(IXH)=FXR
      FXH=FXR
C  CONTRACTION IS AT STATEMENT NO 35
      GO TO 35
C  CONTRACTION WAS SUCESSFUL
   17 DO 18 J = 1,N
      X(J,IXH)=XC(J)
      XH(J)=XC(J)
   18 CONTINUE
      F(IXH)=FXC
      GO TO 11
    3 WRITE(6,600)
  600 FORMAT(1H0,*CONCLUSION OF SEARCH*)
      IF (NWRIT .LE. 0) GO TO 1000
      WRITE(6,605)
      DO 54 IL=1,N1
      WRITE(6,603)(X(IM,IL),IM=1,N )
   54 CONTINUE
      WRITE(6,606)
      WRITE(6,603)(F(KK),KK=1,N1)
      WRITE(6,700)
  602 FORMAT(1H ,7E12.4)
  700 FORMAT(1H ,*XH,XS,XL,XR,XE,XC,XU*//)
      WRITE(6,602)(XH(K),XS(K),XL(K),XR(K),XE(K),XC(K),XU(K),K=1,N)
 1000 CONTINUE
      WRITE(6,601)NTRY,NMAX,FSTOP,EPS
  601 FORMAT(1H ,*NO. OF FUNCTION EVALUATIONS =  *,I5//,
     1  *  MAXIMUM PERMITTED  =   *,I5//,
     1  *  ERROR   =  *,E20.5//,
     1  *  MAXIMUM ERROR REQUIRED  =   *,E20.5)
      DO 820 I=1,N
      X(I,1)=XL(I)
  820 CONTINUE
      RETURN
      END
```

VI.2 EXPERIMENTAL DESIGN

Those computer subroutines which are used in the experimental design problem and reported here are:

(i) TST (Main Program),
(ii) FUN,
(iii) EVDET,
(iv) MINI,
(v) SEARCH,
(vi) TEST .

The CHEMIST subroutine package, the utility program "MINVSE," and the subroutine "MODEL" are all used in the same manner as described in the previous section.

```
C EXPERIMENTAL DESIGN TST - MAIN PROGRAM TO DIRECT PARAMETER SEARCH
      PROGRAM TST(INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT)
      REAL    KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS
      COMMON AIJ(460), IROW(460), JCOL(460)                             NZSC0100
      REAL AIJ,NAME,MWW                                                 NZSC0110
      COMMON /HOLB/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK, NZSC0130
     1  H2O,HPLUS
      COMMON /REAL8/ RRB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,
     1   XSTART,BARMIN,SLACKS,ALITER,RT,B(60),PIE(75),V1(75),V2(75),    NZSC0170
     2   V3(75),V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170),  NZSC0180
     3   XBAR(25),R(75,75),FE,FE2,ERMB,AEMB,ERMA,AEMA                   NZSC0190
      COMMON /INTGR/ M,MEND,NCOMP,N,NIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,NZSC0210
     1   KE,MAXM,MAXP,MARK,MAXMD,NCYCLE,NBSTAR,NPF,                     NZSC0220
     2   NAIJ,MAXAIJ,IOPT,MTOG,MARITH,KL(26),JCOMP(170),NEMB,NEMA       NZSC0230
      EQUIVALENCE (N,NTOT)                                              NZSC0240
      INTEGER PF                                                        NZSC0250
      COMMON /TOGL/ IARITH,IFIND,INTITL,INSOLV,IJOHN,ILP,IMATRX,IPUSH,  NZSC0270
     1                 IROWS,ISCALE
      COMMON /MOLER/CMW(60),Z1(60),DENSP,DENS,MWW,SMW(170),Z(170),      NZSC0290
     ITOT,ISTOP,K,JI,JT,A1,A2,AC(170)
      COMMON /MOD/ STOR(30,30),XIVX(10,10),EC(15,30),PR(7,30),PD(7,10),
     APDI(7,10),CPRINT
      DIMENSION F(60),G(60),SP(60),AB(20)
      DATA (AB(I), I=1,13) /13*0./
C LOWER CONSTRAINTS
      DATA (F(I), I=1,39) /39*1.E-06/
C UPPER CONSTRAINT
      DATA (G(I), I=1,39) /39*1.E-03/
C CPRINT PRINT CONTROL FOR MOLAR CONC. IN SUBROUTINE MODEL
      NX = 13
      CALL START
      CALL INPUT
      READ(5,100) (CMW(I), I = 1,M)
      READ(5,100) (Z1(I), I = 1,M)
      READ(5,100) DENSP,MWW,A1,A2
      CALL MWCALC(5HLIQUID,1.,MWC)
      DO 7,I=1,37,3
C  SP  SEARCH PARAMETERS (INDEPENDENT VARIABLES FOR EXPERIMENTS)
 7    READ(5,101) SP(I+2),SP(I+1),SP(I)
 101  FORMAT(2E10.3,40X,E10.3)
C  TRANSFORM SEARCH PARAMETERS TO LIE WITHIN THE UPPER AND LOWER CONSTRAINTS
      DO 5 I=1,39
      SP(I) = (SP(I)-F(I))/(G(I)-F(I))
      SP(I) = SQRT(SP(I))
      SP(I) = ASIN(SP(I))
 5    CONTINUE
      DO 1 I=1,NX
      DO 1 J = 1,N
 1    STOR(J,I) = XSTART
```

```
      CPRINT = 0.
C  INITATE SEARCH FOR EXPERIMENTS
      CALL MINI(SP)
      CPRINT = 1.
      CALL FUN(SP,DET)
      CALL PAGE
      WRITE(6,200)
C SET OF INDEPENDENT VARIABLES FOR NEW EXPERIMENT
      DO 6 I=1,NX
      EC(7,I) = EC(7,I) - AB(I)
 6    WRITE(6,201) EC(3,I),EC(5,I),EC(7,I)
      WRITE(6,202)
C XTVX  INVERSE PARAMETER COVARIANCE MATRIX
      WRITE(6,2 3) ((XTVX(I,J), J=1,3), I=1,3)
C  DET SEARCH CRITERION D
      WRITE(6,207) DET
C  PREDICTED RESPONSE FOR THE PROPOSED EXPERIMENTS
      DO 2 I=1,NX
      WRITE(6,204) I
      WRITE(6,205) (PR(J,I), J=1,3)
      WRITE(6,206) KN(15),KN(16),STOR(15,I),STOR(16,I)
 2    CONTINUE
      STOP
 100  FORMAT(8F10.3)
 200  FORMAT(///10X,*LEVELS OF THE INDEPENDENT VARIABLES*,//10X,*LANTHAN
     1UM.      PYROPHOSPHATE HCL*,/30X,*(MOLES/L)*)
 201  FORMAT(/10X,3(1PE10.3,5X))
 202  FORMAT(///10X,*COVARIANCE MATRIX*,/)
 203  FORMAT(/3(5X,1PE10.3,5X))
 204  FORMAT(///10X,*PREDICTED CONC. FOR EXPT NO.  *,I2)
 205  FORMAT(///10X,*LANTHANUM   PYROPHOSPHATE    PH*,/30X,*(MG/L)*,/10X
     A,1PE10.3,3X,E10.3,4X,0PF6.3)
 206  FORMAT(//10X,*SOLID PHASES - MOLES*,/10X,2(A6,6X),/10X,2(1PE10.3,2
     AX))
 207  FORMAT(///10X,*VALUE OF THE DETERMINANT  *,1PE10.3)
      END
C PROGRAM TO INTRODUCE OPERATING VARIABLES FOR SEARCH PROCEDURE
      BLOCK DATA
      COMMON/ONE/ Y(30),S(30),FX,FY,STEP,TOL,ACC
      COMMON /THREE/ N,NFUNCT,NDRV,ITER,INDIC,IPRINT
      DATA N,NFUNCT,NDRV,ITER,INDIC,IPRINT/39,0,0,0,2,1/
      DATA STEP,TOL,ACC/0.10,0.01,0.01/
      END
C  PROGRAM FUN CALCULATES THE OBJECTIVE FUNCTION FOR THE SEARCH PROCEDURE
      SUBROUTINE FUN(Z,DET)
C Z SEARCH PARAMETERS
C  DET SEARCH CRITERION
      COMMON /MOD/ STOR(30,30),XTVX(10,10),EC(15,30),PR(7,30),PD(7,10),
     APDI(7,10),CPRINT
      COMMON /THREE/ N,NFUNCT,NDRV,ITER,INDIC,IPRINT
      DIMENSION Z(60),Y(10,10),T(60),F(60),G(60),PXTVX(5,5)
      DIMENSION VAR(5),EV(2,2),A(2,3),B(3,2),N1(8),WORK(2),C(3,3)
C LOWER CONSTRAINTS
      DATA (F(I), I=1,39) /39*1.E-06/
C UPPER CONSTRAINT
      DATA (G(I), I=1,39) /39*1.E-03/
C SET THE INITIAL VALUE OF THE XTVX MATRIX  PREVIOUS MATRIX PXTVX
```

```
C ZERO IF NO INITIAL EXPERIMENTS
      DATA((PXTVX(I,J), J=1,3), I=1,3) /9*0./
      NE=0  $  NMR=2  $  MNIV=3  $  NP=3
      DO 12 I=1,NP
      DO 12 J=1,NP
 12   XTVX(I,J) = PXTVX(I,J)
      NF = N + 1 - MNIV
      DO 1 I=1,NF,MNIV
      NE = NE + 1
      T(I) = F(I) + (G(I)-F(I))*SIN(Z(I))*SIN(Z(I))
      T(I+1) = F(I+1) + (G(I+1)-F(I+1))*SIN(Z(I+1))*SIN(Z(I+1))
      T(I+2) = F(I+2) + (G(I+2)-F(I+2))*SIN(Z(I+2))*SIN(Z(I+2))
      EC(1,NE) = 0.
      EC(2,NE) = 5.*T(I+2)
      EC(3,NE) = T(I+1)
      EC(4,NE) = 0.
      EC(5,NE) = T(I+2)
      EC(6,NE) = 3.*T(I+1)
      EC(7,NE) = T(I)
C  ESTIMATE THE PARTIAL DERIVATIVES FOR THE CURRENT ESTIMATES OF THE SEARCH PARA
C  -METERS
      CALL MODEL(NE)
C CALCULATE THE EFFECTIVE ERRORS
C ESTIMATES OF THE PRIME ERRORS IN THE OBSERVED RESPONSE
      VAR(1) = (.1071*PR(1,NE))**2
      VAR(2) = (0.0318*PR(2,NE))**2
C ESTIMATES OF THE ERRORS IN THE INDEPENDENT VARIABLES
      VAR(3)=1.E-10  $  VAR(4)=1.E-12  $  VAR(5)=1.E-12
      DO 3 J = 1,NMR
      DO 3 K = 1,NMR
      EV(K,J) = 0.
C  EV EFFECTIVE ERROR ESTIMATES
C PDI PARTIAL DERIVATIVES OF THE MODEL RESPONSE WRT INDEPENDENT VARIABLES
      DO 4 L=1,MNIV
 4    EV(K,J) = EV(K,J) + PDI(J,L)*PDI(K,L)*VAR(NMR+L)
      IF(K.EQ.J) EV(K,J) = EV(K,J) + VAR(J)
 3    CONTINUE
      IF(CPRINT.GT.0.) WRITE(6,201) ((EV(II,JJ), II=1,2), JJ=1,2)
      CALL MIRVSE(EV,NMR,NMR,1.E-20,IERR,N1,WORK)
      IF(CPRINT.GT.0.) WRITE(6,201) ((EV(II,JJ), II=1,2), JJ=1,2)
 201  FORMAT(/1X,*COVARIANCE MATRIX*,/2(5X,1PE10.3,5X))
      DO 5 J =1,NMR
      DO 5 K =1,NP
 5    A(J,K) = PD(J,K)
      CALL GTPRD(A,EV,B,NMR,NP,NMR)
      CALL GMPRD(B,A,C,NP,NMR,NP)
      IF(CPRINT.GT.0.) WRITE(6,202) ((C(K,J), J=1,3), K=1,3)
 202  FORMAT(/10X,* C - MATRIX*,/3(5X,1PE10.3,5X))
      DO 6 J = 1,NP
      DO 6 K = 1,NP
C ADD CONTRIBUTION FROM EACH EXPERIMENT
 6    XTVX(J,K) = C(J,K) + XTVX(J,K)
 1    CONTINUE
      DO 7 I=1,NP
      DO 7 J=1,NP
 7    Y(I,J) = XTVX(I,J)
C EVALUATE THE DETERMINANT
```

```
      CALL EVDET(Y,NP,DET)
      WRITE(6,200) (T(I), I=1,N)
  200 FORMAT(/1 X,*CURRENT SEARCH VARIABLES*,/6(5X,1PE10.3,5X))
      DET = ABS(1./DET)
      NFUNCT = NFUNCT + 1
      WRITE(6,203) DET
  203 FORMAT(/10X,*DETERMINANT VALUE  *,1PE10.3)
      RETURN
      NFUNCT = NFUNCT + 1
      RETURN
      END
C PROGRAM TO EVALUATE A DETERMINANT
      SUBROUTINE EVDET(D,N,DET)
C  D DETERMINANT TO BE EVALUATED
C  N ORDER OF THE DETERMINANT
C  DET DETERMINAT VALUE
      DIMENSION D(10,10),A(10,10)
      IF(D(1,1).EQ.0.) GO TO 5
      DET = 1.
      NA = N-1
      DO 1 I = 1,NA
      L = I + 1
      DO 2 J = 1,N
      DO 2 K = L,N
  2   A(K,J) = D(K,J) - (D(I,J)/D(I,I))*D(K,I)
      DO 3 J = 1,N
      DO 3 K = L,N
  3   D(K,J) = A(K,J)
  1   CONTINUE
      DO 4 I = 1,N
  4   DET = DET*D(I,I)
      WRITE(6,203) DET
  203 FORMAT(/10X,*DETERMINANT VALUE  *,1PE10.3)
  6   RETURN
  5   WRITE(6,201)
  201 FORMAT(//10X,*THE PIVOT ELEMENT IS ZERO - DETERMINANT IS NOT EVALU
     1ATED*)
      GO TO 6
      END
C PROGRAM TO CARRY OUT SEARCH FOR PARAMETERS BASED ON POWELL'S ALGORITHM
      SUBROUTINE MINI(X)
C  X SEARCH PARAMETERS
C  DIRECT METHOD OF SEARCH
C  SUBROUTINE TEST MUST BE PROVIDED FOR CONVERGENCE TESTING
C
      COMMON/ONE/ Y(30),S(30),FX,FY,STEP,TOL,ACC
      COMMON /TWO/ DIRECT(30,30),DUM(30),BEFORE(30),FIRST(30)
      COMMON /THREE/ N,NFUNCT,NDRV,ITER,INDIC,IPRINT
      DIMENSION X(30),W(30),SECND(30)
      EQUIVALENCE   (W,SECND)
C *** N = THE NUMBER OF VARIABLES.
C     ICONVG = THE FINAL CONVERGENCE TEST DESIRED.
C            =.1, TERMINATE AS SOON AS TESTING IS SATISFIED.
C            = 2, AS SOON AS THE TESTING CRITERIA ARE SATISFIED INCREASE
C              * ALL THE VARIABLES BY 10*ACC AND SOLVE PROBLEM AGAIN.
C     THEN PERFORM A LINE SEARCH BETWEEN THE SOLUTIONS IF DIFFERENT
C     SOLUTIONS ARE DEEMED TO BE FOUND.
C     STEP = THE INITIAL STEP SIZE.
C     ACC = THE REQUIRED ACCURACY IN THE FUNCTION AND VECTOR VALUES.
```

```
C    INSERT IPRINT = 1 FOR COMPLETE PRINT OUT OR IPRINT = 2
C   1 ANSWER ONLY
C INDIC MUST BE SET TO 2
      INDIC=2
      ICONVG=1
      ITER=0,
      N1=N-1
      NTRY=1
      STEPA=STEP
C *** SET UP THE INITIAL DIRECTION MATRIX (USING UNIT VECTORS).
      DO 2  I=1,N
      DO 1  J=1,N
1     DIRECT(J,I) = 0.
    2 DIRECT(I,I)=1.
C *** EVALUATED THE FUNCTION AT THE INITIAL VARIABLE VALUES.
  100 CALL FUN(X,FX)
      WRITE(6,2000) ITER,NFUNCT,FX,(X(I), I=1,N)
 2000 FORMAT(/1 X,*STAGE  NO. EVALUATIONS  FUNCTION VALUE*,/12X,I2,13X,I
     A5,3X,1PE12.5,/10X,*SEARCH VARIABLES*,/6(5X,E10.3,5X))
      GO TO 301
C *** SAVE THE FINAL FUNCTION VALUE (F1) AND THE FINAL VARIABLE VALUES
C     (BEFORE) FROM THE PREVIOUS CYCLE.
    3 ITER=ITER+1
      IF(IPRINT.EQ.1) WRITE(6,2000)ITER,NFUNCT,FX,(X(I), I=1,N)
  301 F1=FX
      DO 4  I=1,N
    4 BEFORE(I)=X(I)
      SUM=0.
C     AT THE END OF THE CYCLE, SUM WILL CONTAIN THE MAXIMUM CHANGE IN
C     THE FUNCTION VALUE FOR ANY SEARCH DIRECTION, AND ISAVE INDICATES
C     THE DIRECTION VECTOR TO WHICH IT CORRESPONDS.
      DO 9  I=1,N
C     S CONTAINS THE INITIAL STEP SIZES IN THE I-TH DIRECTION.
      DO 5  J=1,N
    5 S(J)=DIRECT(J,I)*STEP
C     FIND THE MINIMUM IN THE I-TH DIRECTION, AND THE CHANGE IN FUNCTION
C     VALUE.
      CALL SEARCH(X)
      IF(IPRINT.EQ.1) WRITE(6,2500)
 2500 FORMAT(/10X,*CURRENT SEARCH VARIABLES AFTER GOLDEN SECTION*)
      IF(IPRINT.EQ.1T WRITE(6,2000)ITER,NFUNCT,FY,(Y(J), J=1,N)
      A=FX-FY
      IF(A-SUM) 7,7,6
    6 ISAVE=I
      SUM=A
C     TRANSFER THE NEW FUNCTION AND VARIABLE VALUES TO FX AND X.
    7 DO 8  J=1,N
    8 X(J)=Y(J)
      WRITE(6,2600) SUM,ISAVE
 2600 FORMAT(//10X,*SEARCH CONSTANTS - SUM  *,1PE10.3,*  ISAVE  *,I2)
    9 FX=FY
C *** NOW INVESTIGATE WHETHER A NEW SEARCH DIRECTION SHOULD BE INCORPOR-
C     ATED INSTEAD OF THE ISAVE DIRECTION.
      F2=FX
      DO 10  I=1,N
   10 W(I)=2.0*X(I)-BEFORE(I)
      CALL FUN(W,F3)
```

```
      A=F3-F1
      IF(A) 11,19,19
   11 A=2.0*(F1-2.0*F2+F3)*((F1-F2-SUM)/A)**2
      IF(A-SUM) 12,19,19
C *** A NEW SEARCH DIRECTION IS REQUIRED. FIRST REMOVE ROW ISAVE.
   12 IF(ISAVE-N) 13,15,15
   13 DO 14  I=ISAVE,N1
      II=I+1
      DO 14  J=1,N
   14 DIRECT(J,I)=DIRECT(J,II)
C     SET THE N-TH DIRECTION VECTOR EQUAL TO THE NORMALISED DIFFERENCE
C     BETWEEN THE INITIAL AND FINAL VARIABLE VALUES FOR LAST CYCLE.
   15 A=0.
      DO 16  J=1,N
      DIRECT(J,N)=X(J)-BEFORE(J)
   16 A=DIRECT(J,N)**2+A
      A=1.0/SQRT(A)
      DO 17  J=1,N
      DIRECT(J,N)=DIRECT(J,N)*A
   17 S(J)=DIRECT(J,N)*STEP
      CALL SEARCH(X)
      FX=FY
      DO 18  I=1,N
   18 X(I)=Y(I)
C *** TEST FOR CONVERGENCE.
   19 CALL TEST(F1,FX,BEFORE,X,FLAG,N,ACC)
      IF(FLAG) 22,20,20
C *** CONVERGENCE NOT YET ACHEIVED. COMPUTE A NEW STEP SIZE AND
C     GO BACK TO 3.
   20 IF(F1-FX)121,120,120
  121 STEP=-0.4*SQRT(ABS(F1-FX))
      GO TO 123
  120 STEP=0.4*SQRT(F1-FX)
 123  IF(STEPA.GE.STEP.AND.FLAG.GT.0.) GO TO 3
      IF(STEPA.LT.STEP) STEP = STEPA
      IF(FLAG.GT.0.) GO TO 3
      WRITE(6,2100) STEP
 2100 FORMAT(/10X,*THE STEPSIZE FOR THE NEXT STAGE  *,1PE10.3)
C *** CONVERGENCE ACHEIVED. IF ICONVG=2, INCREASE ALL VARIABLES BY
C     10*ACC AND GO BACK TO 3.
   22 GO TO (23,24),ICONVG
   23 RETURN
   24 GO TO (25,27),NTRY
   25 NTRY=2
      DO 26  I=1,N
      FIRST(I)=X(I)
   26 X(I)=X(I)+ACC*10.
      FFIRST=FX
      GO TO 100
C *** CONVERGENCE ATTAINED USING TWO DIFFERENT STARTING POINTS. CONSTRUC
C     UNIT VECTOR BETWEEN SOLUTIONS AND SEARCH DIRECTION FOR A MINIMUM.
   27 SECOND=FX
      A=0.
      DO 28  I=1,N
      SECND(I)=X(I)
      S(I)=FIRST(I)-SECND(I)
   28 A=A+S(I)**2
```

```
      IF(A) 23,23,29
   29 A=STEP/SQRT(A)
      DO 30  I=1,N
   30 S(I)=S(I)*A
      CALL SEARCH(X)
C *** TEST IF NEW POINT IS SUFFICIENTLY CLOSE TO EITHER OF THE TWO
C     SOLUTIONS. IF SO RETURN.
      CALL TEST(FFIRST,FY,FIRST,Y,FLAG,N,ACC)
      IF(FLAG) 32,32,31
   31 CALL TEST(FSECND,FY,SECND,Y,FLAG,N,ACC)
      IF(FLAG) 32,32,34
   32 DO 33  I=1,N
   33 X(I)=Y(I)
      FX=FY
      RETURN
C *** FINAL SOLUTION NOT ACCURATE ENOUGH.  REPLACE THE FIRST DIRECTION
C     VECTOR BY INTER-SOLUTION VECTOR (NORMALISED) AND RECYCLE
   34 A=A/STEP
      DO 35  I=1,N
      DIRECT(I,1)=(FIRST(I)-SECND(I))*A
   35 FIRST(I)=SECND(I)
      GO TO 3
      END
C PROGRAM TO CALCULATE THE OPTIMUM STEPSIZE BASED ON THE GOLDEN SECTION METHOD
      SUBROUTINE SEARCH(X)
C  UNIDIMENSIONAL SEARCH USING GOLDEN SECTION.  VERSION 2, MOD 4.
      COMMON/ONE/ Y(30),S(30),FX,FY,STEP,TOL,ACC
      COMMON /TWO/ H(30,30),DELX(30),DELG(30),GX(30)
      COMMON /THREE/ N,NFUNCT,NDRV,ITER,INDIC,IPRINT
      DIMENSION X(30),Z(30),W(30),P(30),R(30),DIFF(30),SS(30)
      DATA F1/0.618033989/
C  P=OLDEST OF LAST THREE POINTS
C  Z=MIDDLE POINT
C  W=CURRENT POINT
      NTRIES=0
      NTOL=0
C  TOL=SQUARED NORM OF VECTOR FROM W TO Z WHICH MUST BE ACHIEVED FOR
C     CONVERGENCE
      NTIMES=0
C  USE THE PARAMETER INDIC TO INDICATE HOW THE SEARCH VECTOR LENGTH
C  SHOULD BE SCALED.
C     INDIC=2  DO NOT SCALE.  TAKE LENGTH GIVEN BY MINI CALCULATION
C     INDIC=1  SCALE ONLY IF THE LENGTH OF THE LAST STEP WAS SHORTER THAN
C              THE LENGTH OF THE SEARCH VECTOR.  SCALE TO LENGTH OF LAST STEP
C     INDIC=ANYTHING BUT 1 OR 2 RESULTS IN SCALING TO LENGTH OF LAST STEP.
      IF(INDIC.EQ.2.OR.ITER.EQ.0) GO TO 4
C  NORMALIZE THE SEARCH VECTOR TO THE LENGTH USED ON THE PREVIOUS STEP.
      DXNORM=0.
      SNORM=0.
      DO 2 I=1,N
      DXNORM=DXNORM+DELX(I)*DELX(I)
    2 SNORM=SNORM+S(I)*S(I)
      IF(INDIC.EQ.1.AND.DXNORM.GE.SNORM) GO TO 4
      DXNORM=SQRT(DXNORM)
      SNORM=SQRT(SNORM)
      RATIO=DXNORM/SNORM
      DO 3 I=1,N
    3 SS(I)=S(I)*RATIO
      GO TO 10
```

```
C  MAINTAIN THE INTEGRITY OF THE SEARCH VECTOR BY CONSTRUCTING AN IDENTICAL
C  VECTOR AND OPERATING ON IT.
4      DO 5 I=1,N
5      SS(I)=S(I)
C***BRACKET THE MINIMUM IN THE S DIRECTION
C  TAKE STEP FROM ORIGINAL POINT
10     DO 20 I=1,N
       Z(I)=X(I)
20     W(I)=X(I)+SS(I)
       FZ=FX
       NTIMES=NTIMES+1
       CALL FUN(W,FW)
       IF(FW-FZ) 30,70,50
C  CONTINUE SEARCH IN SAME DIRECTION
30     DO 40 I=1,N
       P(I)=Z(I)
       Z(I)=W(I)
       S(I)=2.*SS(I)
40     W(I)=W(I)+SS(I)
       FP=FZ
       FZ=FW
       NTIMES=NTIMES+1
       CALL FUN(W,FW)
       IF(FW-FZ) 30,70,120
C  FW.GT.FZ, DECIDE WHETHER TO RECERSE SEARCH DIRECTION
50     IF(NTIMES.NE.1) GO TO 120
C  REVERSE SEARCH DIRECTION
       DO 60 I=1,N
       SS(I)=-SS(I)
60     P(I)=W(I)
       FP=FW
       GO TO 10
C  FZ=FW, CHECK MIDPOINT
70     DO 80 I=1,N
80     R(I)=(Z(I)+W(I))/2.
       NTIMES=NTIMES+1
       CALL FUN(R,FR)
       MIN=1
       IF(FR-FZ) 140,300,90
90     IF(NTIMES.NE.2) GO TO 110
C  REVERSE SEARCH DIRECTION
       DO 100 I=1,N
       SS(I)=-SS(I)
100    P(I)=R(I)
       FP=FR
       GO TO 10
C  R AND P BRACKET Z AND THE MINIMUM
110    DO 115 I=1,N
       W(I)=R(I)
       R(I)=Z(I)
115    Z(I)=P(I)
       MIN=1
       FW=FR
       FR=FZ
       FZ=FP
       GO TO 140
C  P AND W BRACKET Z AND THE MINIMUM
```

```
 120  DO 130 I=1,N
      R(I)=Z(I)
 130  Z(I)=P(I)
      MIN=1
      FR=FZ
      FZ=FP
C***GOLDEN SEARCH)  Z AND W BRACKET THE MINIMUM
 140  WZNORM=0.
      DO 145 I=1,N
      DIFF(I)=W(I)-Z(I)
 145  WZNORM=WZNORM+DIFF(I)*DIFF(I)
      IF(WZNORM.LT.TOL) GO TO 290
 146  DO 150 I=1,N
      SECT=F1*DIFF(I)
      P(I)=Z(I)+SECT
 150  R(I)=W(I)-SECT
      CALL FUN(P,FP)
      CALL FUN(R,FR)
 160  IF(FR-FP) 170,230,200
C  REPLACE W BY P AND P BY R
 170  WZNORM=0.
      DO 180 I=1,N
      W(I)=P(I)
      P(I)=R(I)
      DIFF(I)=W(I)-Z(I)
      WZNORM=WZNORM+DIFF(I)*DIFF(I)
 180  R(I)=W(I)-F1*DIFF(I)
      FW=FP
      FP=FR
      IF(WZNORM.LT.TOL) GO TO 320
      CALL FUN(R,FR)
      GO TO 160
C  REPLACE Z BY R AND R BY P
  00  WZNORM=0.
      DO 210 I=1,N
      Z(I)=R(I)
      R(I)=P(I)
      DIFF(I)=W(I)-Z(I)
      WZNORM=WZNORM+DIFF(I)*DIFF(I)
  10  P(I)=Z(I)+F1*DIFF(I)
      FZ=FR
      FR=FP
      IF(WZNORM.LT.TOL) GO TO 300
      CALL FUN(P,FP)
      GO TO 160
C  FP=FR, CHECK MIDPOINT
  30  DO 240 I=1,N
  40  Y(I)=(P(I)+R(I))/2.
      CALL FUN(Y,FY)
      IF(FY-FP) 250,340,270
C  P AND R BRACKET THE MINIMUM (YIS BRACKETED)
  50  DO 260 I=1,N
      Z(I)=R(I)
      W(I)=P(I)
  60  R(I)=Y(I)
      FZ=FR
      FW=FP
```

```
      FR=FY
      MIN=1
      GO TO 140
C  THERE ARE TWO MINIMA BETWEEN Z AND W.  ARBITRARILY PICK THE INTERVAL
C  BETWEEN Y AND W (WHICH INCLUDES P)
 70   DO 280 I=1,N
280   Z(I)=Y(I)
      FZ=FY
      MIN=2
      GO TO 140
C  BRACKET ON THE MIN IS SUFFICIENTLY SMALL
 90   GO TO (300,320), MIN
C  R IS THE POINT INSIDE THE BRACKET
300   DO 310 I=1,N
310   Y(I)=R(I)
      FY=FR
      GO TO 340
C  P IS THE POINT INSIDE THE BRACKET
320   DO 330 I=1,N
330   Y(I)=P(I)
      FY=FP
340   CONTINUE
      IG = 1
      DO 345 I=1,N
      IF(X(I).NE.Y(I)) IG=2
 345  CONTINUE
      GO TO (350,346),IG
 346  IF(FY.GE.FX) GO TO 370
      IF(IPRINT.NE.1) RETURN
      IF(NTOL.NE.3) WRITE(6,3000) NTOL
      IF(NTRIES.NE.0) WRITE(6,3100)
3000  FORMAT(1X,*TOLERANCE REDUCED *,I1,* TIME(S*)
3100  FORMAT(1X,*SECOND TRY.*)
      RETURN
C**TAKE CARE OF PATHALOGICAL CONDITONS
C  AT THE PRESENT TOLERANCE LEVEL NO POINT CAN BE FOUND WHICH
C  IS BETTER THIN THE ENTERING POINT.  REDUCE TOL BY A FACTOR OF 100.
350   IF(NTOL.EQ.5) GO TO 360
      NTOL=NTOL+1
      TOL=TOL/100.
      GO TO 146
C  PRINT MESSAGE AND RETURN
360   IF(IPRINT.NE.1) GO TO 376
      IF(NTRIES.NE.0) GO TO 375
      WRITE(6,2000) TOL
2000  FORMAT(1X,*THE TOLERANCE HAS BEEN REDUCED 5 TIMES TO A CURRENT VAL
     AUE OF*,E15.8,*.*,/,
     B1X,  *A POINT BETTER THAN THE ENTERING POINT CANNOT BE FOUND AT TH
     CIS LEVEL OF TOLERANCE.  THE ENTERING POINT IS BEING RETURNED.*)
      GO TO 376
C** FY.GT.FX, FIND A BRACKET EXCLUDING THE VALLEY CONTAINING Y.
370   IF(NTRIES.EQ.0) GO TO 380
      IF(NTOL.LT.5) GO TO 350
 375  WRITE(6,2100)
      WRITE(6,3000) NTOL
2100  FORMAT(1X,*A POINT WAS FOUND SUCH THAT FY WAS GREATER THAN FX.  A
     BSECOND ATTEMPT TO FIND A POINT WITH A FUNCTION VALUE LESS THAN FX
```

```
     CFAILED.*)
376   IF(S(1).NE.-GX(1) .OR.(FY.LT.FX)) RETURN
      WRITE(6,2200)
2200  FORMAT(* SEARCH FAILED ON A GRADIENT STEP.  JOB TERMINATED*)
      WRITE(6,2300) ITER,NFUNCT,FY,(Y(I), I=1,N)
 2300 FORMAT(/1 X,*STAGE  NO. EVALUATIONS  FUNCTION VALUE*,/12X,I2,13X,I
     A5,3X,1PE12.5,/10X,*SEARCH VARIABLES*,/6(5X,E10.3,5X))
      STOP
C  LOOK FOR A BRACKET NEAR X ON THE SIDE OPPOSITE FROM Y.
380   NTRIES=1
      DO 390 I=1,N
      Z(I)=X(I)
      SS(I)=(X(I)-Y(I))/20.
390   W(I)=X(I)+SS(I)
      FZ=FX
      CALL FUN(W,FW)
      IF(FW-FZ) 30,400,450
C  FZ=FW, CHECK MIDPOINT
400   DO 410 I=1,N
410   P(I)=(Z(I)+W(I))/2.
      CALL FUN(P,FP)
      IF(FP-FZ) 420,320,430
C FZ.GT.FP AND FW.GT.FP.  W AND Z FORM A BRACKET
420   MIN=2
      GO TO 140
C  FP.GT.FZ, P IS A BRACKET WITH THE MINIMUM BETWEEN P AND Y
430   DO 440 I=1,N
440   W(I)=P(I)
      FW=FP
C  FW.GT.FZ, W IS A BRACKET WITH THE MINIMUM BETWEEN W AND Y
C  CHECK MIDPOINT OF Y AND W
450   DO 460 I=1,N
      Z(I)=Y(I)
460   P(I)=(Z(I)+W(I))/2.
      FZ=FY
470   CALL FUN(P,FP)
      IF(FP.LE.FZ) GO TO 490
C  TRY AGAIN
      DO 480 I=1,N
      Z(I)=P(I)
480   P(I)=(W(I)+Z(I))/2.
      FZ=FP
      GO TO 470
C  P IS IN A VALLEY DIFFERENT FROM THE ONE CONTAINING Y.
C  CHECK WHETHER P AND W FORM A BRACKET
490   DO 500 I=1,N
500   R(I)=(P(I)+W(I))/2.
      CALL FUN(R,FR)
      IF(FR.GE.FW) GO TO 560
      IF(FR.GE.FP) GO TO 520
C  P AND W FORM A BRACKET
505   DO 510 I=1,N
510   Z(I)=P(I)
      FZ=FP
      MIN=1
      GO TO 140
C  FR.LT.FW, FR.GE.FP.  HENCE LOOK FOR A BRACKETING VALUE BETWEEN P AND Z.
```

```
520   DO 530 I=1,N
      R(I)=P(I)
 530  P(I) = (P(I) + Z(I))/2.
      FR=FP
540   CALL FUN(P,FP)
      IF(FP.LE.FZ) GO TO 490
C  FP.GT.FZ.  APPARENTLY Z IS IN THE SAME VALLEY WITH Y.
      DO 550 I=1,N
      Z(I)=P(I)
550   P(I)=(R(I)+Z(I))/2.
      FZ=FP
      GO TO 540
C  FR.GE.FW
560   IF(FR.LT.FP) GO TO 505
C  FR.GE.FP, R AND W FORM A BRACKET
      DO 570 I=1,N
570   Z(I)=R(I)
      FZ=FR
      GO TO 146
      END
C PROGRAM TO TEST CONVERGENCE  CRITERIA
      SUBROUTINE TEST(FI,FF,RI,RF,FLAG,N,ACC)
C  THIS SUBROUTINE IS PECULIAR TO THE POWELL METHOD OF DIRECT SEARCH
      DIMENSION RI(30),RF(30)
      CALL SECOND(TIME)
      WRITE(6,201) TIME
 201  FORMAT(/10X,*TIME ELAPSED AFTER ONE STAGE  *,1PE10.3,*  SECONDS*)
      IF(TIME.GT.220.) GO TO 8
      FLAG=+2.
      IF(ABS(FI)-ACC) 2,2,1
    1 IF(ABS((FI-FF)/FI)-ACC) 3,3,7
    2 IF(ABS(FI-FF)-ACC) 3,3,7
    3 DO 6  I=1,N
      IF(ABS(RI(I))-ACC) 5,5,4
    4 IF(ABS((RI(I)-RF(I))/RI(I))-ACC) 6,6,7
    5 IF(ABS(RI(I)-RF(I))-ACC) 6,6,7
    6 CONTINUE
      FLAG=-2.
    7 RETURN
 8    WRITE(6,200)
 200  FORMAT(/10X,*THE SEARCH HAS BEEN CONCLUDED BECAUSE OF THE TIME DEF
     1AULT - THE CONVERGENCE FLAG HAS BEEN SET*)
      FLAG = 0.
      GO TO 7
      END
```

VI.3 DOSAGE MODEL

As the computer programs, which are used to predict the equilibrium composition in the distilled (Chapter V, Section 1) and wastewater (Chapter V, Section 2) systems, represent less sophisticated versions of the Dosage model, only the latter set of computer programs are listed here. In this section, the programs listed are:

(i) TST (Main Program),
(ii) TAB,
(iii) EXPER.

The subroutine "MODEL" has a form similar to the listing reported in section 1. The program has been modified by substituting the common block /MOD1/ for /MOD/ and the call statement "CALL PHSLV" for "CALL CORR." The Dosage model also calls upon subroutines in the CHEMIST package.

```
          PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5 = INPUT,TAPE6 = OUTPUT)
C DOSAGE MODEL       CALCULATES THE QUANTITY OF LANTHANUM REQUIRED TO MEET
C A SPECIFIC PHOSPHORUS RESIDUAL
C INPUT DATA CONCERNING WATER QUALITY IS EXPRESSED IN THE WIDELY USED UNITS
      REAL   KA,KB,NR,NN,NAM,END,BLANK,H2O,HPLUS
      COMMON AIJ(460), IROW(460), JCOL(460)                             NZSC0100
      REAL AIJ,NAME,MWW                                                 NZSC0110
      COMMON /HOL8/ KA(12),KB(12),NR(60,2),NN(170),NAM(25,2),END,BLANK, NZSC0130
     1   H2O,HPLUS                                                      NZSC0140
      COMMON /REAL8/ BBB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,    NZSC0160
     1   XSTART,BARMIN,SLACKS,ALITER,NT,B(60),PIE(75),V1(75),V2(75),    NZSC0170
     2   V3(75)3V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170),  NZSC0180
     3   XBAR(25),R(75,75),FE,FE4,EMMB,XEMB,EMMA,XEMA                   NZSC0190
      COMMON /INTGR/ M,MEND,NCOMP,N,NIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,NZSC0210
     1   NE,MAXM,MAXP,MAXN,MAXND,NCYCLE,NBSTAR,NPF,                     NZSC0220
     2   NAIJ,MAXAIJ,IOPT,NTOG,MARITH,NE(26),NCOMP(170);NEMB,NEMA,      NZSC0230
      EQUIVALENCE (N,NTOT)                                              NZSC0240
      INTEGER PF                                                        NZSC0250
      COMMON /TOGL/ IARITH,IFIND,INTITL,INSOLV,IOUNN,ILP,IMATRXIIPUSH,  NZSC0270
     1               IROWS,ISCALE
      COMMON/MOLEN/CMW(60),ZI(60),DENSP,DENS,MAW,SMW(170),Z(170D,       NZSC0290
     1TOT,ISTOP,K,JI,JT,A1,A2,AC(170)
      DIMENSION EIV(8),VY(1,7),NM(3)
      COMMON /MODI/ STOR(7082)BPR(7,2),PD(7,10),PDI(7,10),CPRINT
      CALL START
      CALL INPUT
      READ(5,100) (CMW(I), I=1,M)
      READ(5,100) (ZI(I), I=1,M)
      READ(5,100) DENSP,MWW,A1,A2
      CALL MWCALC(6HLIQUID,1.,MWC)
      DO 8 J=1,M
      DO 8 I=1,NX
    8 STOR(J,I) = XSTART
C NPROB NO. OF CASES TO BE TRIED
C NTRY NO. OF ITERATIONS ALLOWED TO ESTIMATE THE DOSAGE IN EACH CASE
      READ(5,101) NPROB,NTRY
  101 FORMAT(2I3)
      DO 55 IJK = 1,NPROB
C SET BMULT(4) TO SOLUTION ACIDITY (MOLES/L H+) OR BMULT(5) TO ALKALINITY (MOLES
C /L OH-) IF KNOWN, OTHERWIZE SET PARAMETERS TO ZERO
C  CRIT TOLERANCE ALLOWED ON PHOSPHATE RESIDUAL CONCENTRATION
      READ(5,100) BMULT(4),BMULT(5),CRIT
      CALL PAGE
      WRITE(6,200)
C  INPUT OF WATER QUALITY PARAMETERS
C  PHOSPHATE DISTRIBUTION (MG/L P) ORTHO-,PYRO,TRIPOLY
      READ(5,100) BBB(7,2),BBB(9,2),BBB(6,2)
```

```
      PT = BBB(7,2) + BBB(9,2) + BBB(6,2)
C  ESTIMATED STANDARD DEVIATION
      READ(5,100) EIV(3),EIV(5),EIV(2)
C  EIV ESTIMATED STANDARD DEVIATIONS OF THE INPUT PARAMETERS
      WRITE(6,201) BBB(7,2),EIV(3),BBB(9,2),EIV(5),BBB(6,2),EIV(2),PT
C  HARDNESS AS MG/L CACO3 AND MG/L MGCO3
      READ(5,100) BBB(10,2),BBB(11,2)
C  ESTIMATED STANDARD DEVIATIONS
      READ(5,100) EIV(6),EIV(7)
      WRITE(6,202) BBB(10,2),EIV(6),BBB(11,2),EIV(7)
C  TOTAL INORGANIC CARBON CONCENTRATION MG/L CO3-2
      READ(5,100) BBB(8,2)
C  ESTIMATED STANDARD DEVIATION
      READ(5,100) EIV(4)
      WRITE(6,203) BBB(8,2),EIV(4)
C  CHLORIDE,SODIUM, AND SULPHATE ION CONCENTRATION (MG/L ION)
      READ(5,100) BBB(3,2),BBB(2,2),BBB(12,2)
      READ(5,100) EIV(8)
      WRITE(6,204) BBB(3,2),BBB(2,2),BBB(12,2)
C  EQUILIBRIUM PH VALUE
      READ(5,100) VAL
      WRITE(6,205) VAL
C  REDEFINE THE LAPO4 SOL. PROD. FOR PH VALUES LESS THAN 7
      IF(VAL.LT.7.) C(53) = -47.05
C  CONFIDENCE REGION AT WHICH PHOSPHATE REMOVAL IS SPECIFIED
C SPECIFICATION ALLOWED BETWEEN 55. TO 99.95 PERCENT
C IF NO CONFIDENCE INTERVAL IS DESIRED SET CON TO A NEGATIVE VALUE
      READ(5,100) CON
C  CONVERT INPUT INFORMATION TO MOLES/L
      BBB(2,2) = BBB(2,2)/22997.
      BBB(3,2) = BBB(3,2)/35459.
      BBB(7,2) = BBB(7,2)/30977.
      EIV(3) = (EIV(3)/30977.)**2
      BBB(9,2) = BBB(9,2)/61954.
      EIV(5) = (EIV(5)/61954.)**2
      BBB(6,2) = BBB(6,2)/92931.
      EIV(2) = (EIV(2)/92931.)**2
      BBB(8,2) = BBB(8,2)/60018.
      EIV(4) = (EIV(4)/60018.)**2
      BBB(10,2) = BBB(10,2)/100026.
      EIV(6) = (EIV(6)/100023.)**2
      BBB(11,2) = BBB(11,2)/84338.
      EIV(7) = (EIV(7)/84338.)**2
      BBB(12,2) = BBB(12,2)/96072.
      EIV(8) = (EIV(8)/96072.)**2
      BBB(1,2) = BBB(6,2) + 1.5*BBB(7,2) + BBB(8,2) + BBB(9,2)
      BBB(4,2) = 0.
      BBB(5,2) = 0.
C  SATISFY THE BALANCE OF CHARGES BY THE ADDITION OF NA+ OR CL-
      TC = 0.
      DO 1 I=1,M
    1 TC = TC + BBB(I,2)*Z1(I)
      IF(TC)2,3,4
    2 BBB(2,2) = BBB(2,2) -TC
      GO TO 3
    4 BBB(3,2) = BBB(3,2) + TC
C CALCULATE THE LANTHANUM REQUIREMENT
```

```
 3     BBB(5,2) = 1.666*BBB(6,2) + 1.333*BBB(9,2) + BBB(7,2)
       BBB(5,2) = BBB(5,2)*(PT-1.)/PT
C  ASSUME LANTHINUM ADDED AS CHLORIDE SALT
       BBB(3,2) = 3.*BBB(5,2) + BBB(3,2)
C CALCULATE THE REQUIRED T VALUE
       CALL TAB(CON,THETA)
C  PARTIAL DERIVATIVES USED TO ESTIMATE LANTHANUM DOSAGE
       CALL PAGE
       EIV(1) = 0.
       CPRINT = 0.
       ITRY = 0
 12    IT = 1
       MN=1 $ GO TO 54
 50    RATE = PDI(2,1) + PDI(3,1) + PDI(5,1)
       DELTA = DPT/RATE
       IF(DELTA) 9,6,10
 9     IF(ABS(DELTA).GT.BBB(5,2)) GO TO 11
       GO TO 10
 11    DELTA = DELTA*.75
       GO TO 9
 10    IT = 2
       BBB(5,2) = BBB(5,2) + DELTA
       BBB(3,2) = BBB(3,2) + DELTA*3.
       MN=2 $ GO TO 54
 51    IF(HW(2).LT.HW(1)) GO TO 50
       BBB(5,2) = BBB(5,2) - DELTA/2.
       BBB(3,2) = BBB(3,2) - (DELTA/2.)*3.
       ITRY = ITRY + 1
       IF(ITRY.LT.NTRY) GO TO 12
 6     CPRINT = 1.
       MN=3  $  GO TO 54
 52    J1 = JT + 1.
       J2 = N-1
       WRITE(6,206) (KN(J), J=J1,J2)
       WRITE(6,207) (STOR(J,1), J=J1,J2)
       WRITE(6,208) KN(N),STOR(N,1)
       CALL PAGE
       WRITE(6,209)
       BBB(5,2) = BBB(5,2)*138930.
       WRITE(6,210) BBB(5,2)
       EIV(1) = SQRT(VY(1,1))
       WRITE(6,211) PR(1,1),EIV(1)
       EIV(2) = SQRT(VY(1,2))
       EIV(3) = SQRT(VY(1,3))
       EIV(5) = SQRT(VY(1,5))
       WRITE(6,201) PR(3,1),EIV(3),PR(5,1),EIV(5),PR(2,1),EIV(2)
       PR(6,1) = PR(6,1)*2.496
       EIV(6) = SQRT(VY(1,6))*2.496
       PR(7,1) = PR(7,1)*3.468
       EIV(7) = EIV(7)*3.468
       WRITE(6,202) PR(6,1),EIV(6),PR(7,1),EIV(7)
       EIV(4)  = SQRT(VY(1,4))
       WRITE(6,203) PR(4,1),EIV(4)
       BBB(2,2) = BBB(2,2)*22997.
       BBB(3,2) = BBB(3,2)*35459.
       BBB(12,2) = BBB(12,2)*96072.
       WRITE(6,204)  BBB(2,2),BBB(3,2),BBB(12,2)
```

```
      GO TO 55
54    GO TO 55
54    CALL MODEL(1,VAL)
      CALL EXPER(FIV,1,VY)
      VPT = VY(1,2) + VY(1,3) + VY(1,5)
      PT = PR(2,1) + PR(3,2) + PR(5,1)
      YUL = THETA*SQRT(VPT) + PT
      DPT = 1.-PT
      HQ(IT) = ABS(DPT)
      WRITE(6,212) PT,YUL,VPT
      IF(ABS(DPT.LE.CRIT.AND.NN.LT.3) GO TO 6
6     GO TO (50,51,52),NN
55    CONTINUE
      STOP
100   FORMAT(8F10.3)
200   FORMAT(//10X,*INITIAL INFORMATION ON WATER QUALITY*)
201   FORMAT(//10X,*PHOSPHATE DISTRIBUTION (MG/L P) STANDARD DEVIATION*,
     A/10X,*ORTHOPHOSPHATE*,8X,F7.3,4X,F7.3,/10X,*PYROPHOSPHATE*,9X,F7.3
     B,4X,F7.3,/10X,*POLYPHOSPHATE*,9X,F7.3,4X,F7.3,/10X,*TOTAL PHOSPHAT
     CE*,7X,F7.3)
202   FORMAT(//10X,*HARDNESS*,13X,*(MG/L)*,4X,*STANDARD DEVIATION*,/10X,
     A*CALCIUM CARBONATE   *,F8.3,4X,F7.3,/10X,*MAGNESIUM CARBONATE *,F8
     B.3,4X,F7.3)
203   FORMAT(//10X,*TOTAL INORGANIC CARBON CONCENTRATION  (MG/L CO3) STA
     ANDARD DEVIATION*,/48X,F8.3,4X,F7.3)
204   FORMAT(//10X,*ION CONCENTRATION (MG/L)*,/10X,*SODIUM*,12X,F8.3,/10
     AX,*CHLORIDE*,10X,F8.3,/10X,*SULPHATE*,10X,F8.3)
205   FORMAT(/10X,*FINAL SOLUTION PH       *,F6,3)
206   FORMAT(//2X,*SOLIDS PHASE - MOLES*,5X,8(A6,6X))
207   FORMAT(//25X,8(1PE10.3,2X))
208   FORMAT(//2X,*GAS PHASE - MOLES*,5X,A6,6X,1PE10.3)
209   FORMAT(///10X,*PREDICTED WATER QUALITY OF THE EFFLUENT*)
210   FORMAT(///10X,*REQUIRED LANTHANUM DOSAGE    *,F8.3,*   (MG/L LA+3)*
     A)
211   FORMAT(//10X,*RESIDUAL LANTHANUM*,15X,*STANDARD DEVIATION*,/19X,F8
     A.3,4X,F7.3)
212   FORMAT(//10X,*CURRENT ESTIMATE OF TOTAL PHOSPHATE - UPPER LIMIT -,
     A VARIANCE*,/31X,3(1PE10.3,5X))
      END
      SUBROUTINE TAB(CON,THETA)
C CON CONFIDENCE LEVEL
C THETA T-VALUE (ONE-SIDED)  BASED ON 21 DEGREES OF REEDOM
      DIMENSION A(11),B(11)
      DATA 99.95,95,90,85,80,75,70,65,60,55,50./,B/3.819,1,721,1.323,
     A1.063,0.859,0.686,0.532,0.257,0.127,0./
      DO 1 I=1,11
      IF(CON.LE.A(I)) THETA = B(I)
1     CONTINUE
      RETURN
      END
      SUBROUTINE EXPER(FIV,NE,VY)
      COMMON /MOD1/ STOR(7082),PR(7,2),PD(7,16),PDI(7,10),CPRINT
      DIMENSION VY(1,7),FIV(8),TV(7),VB(16,16),A(7),X(7)
      DATA X/6HLA     ,6HPOLY  ,6HPO4    ,6HCO3    ,6HPYRO  ,6HCA     ,6HMG
     A    /
      DATA ((VB(I,J), J=1,16, I=1,16)/3.022E-03,6.039E-03,3.688E-03,13*0
     A.,
```

```
     B6.039E-03,1.368E-02,7.676E-03,13*0.,
     C3.688E-03,7.676E-03,5.454E-03,13*0.,
     D3*0.,5.227E-02,1.265E-02,3.821E-02,10*0.,
     E3*0.,1.265E-02,1.0[illegible]E-01,2.730E-01,10*0.,
     F3*0.,3.821E-02,2.730E-01,7.467E-01,10*0.,
     G6*0.,2.016E-02,5.665E-02,8*0.,
     H6*0.,5.665E-02,2.545E-01,8*0.,
     I8*0.,4.771E-01,7*0.,
     J9*0.,1.325E-03,6*0.,
     K10*0.,4.771E-01,5*0.,
     L11*0.,1.325,6*0.,
     M12*0.,4.771E-01,3*0.,
     N13*0.,1.325,2*0.,
     O14*0.,4.771E-01,0.,
     P15*0.,1.325/
C CALCULATION OF THE EXPERIMENTAL ERROR DUE TO ANALYTICAL TECHNIQUE
      VY(NE,1) = (.1071*PR(1,NE))**2
      PT = PR(2,NE) + PR(3,NE) + PR(5,NE)
      VPT = (0.0381*PT)**2
      XFRAC = PR(2,NE)/PT
      VY(NE,2) = PT*PT*0.0004 + XFRAC*XFRAC*VPT
      XFRAC = PR(3,NE)/PT
      VY(NE,3) = PT*PT*0.0004 + XFRAC*XFRAC*VPT
      VY(NE,4) = (0.0137*PR(4,NE))**2
      XFRAC = PR(5,NE)/PT
      VY(NE,5) = PT*PT*0.0004 + XFRAC*XFRAC*VPT
      VY(NE,6) = (.025*PR(6,NE))**2
      MNIV=8 + NMR=7 NP = 16
      WRITE(6,101) (X(I), I=1,NMR)
      WRITE(6,100) (VY(NE,I), I=1,NMR)
      DO 1 I = 1,NMR
      TV(I) = 0.
      DO 2 J=1,MNIV
 2    TV(I) = TV(I) + PDI(I,J)*PDI(I,J)*EIV(J)
      VY(NE,I) = VY(NE,I) + TV(I)
 1    CONTINUE
      WRITE(6,102) (X(I), I=1,1NMR)
      WRITE(6,100) (TV(I), I=1,NMR)
C ERROR FROM PARAMETER ESTIMATES
      DO 4 I=1,NMR
      A(I) = 0.
      DO 4 J=1,NP
      DO 4 L=1,NP
 4    A(I) = A(I) + PD(I,J)*PD(I,L)*VB(J,L)
      WRITE(6,103) (X(I), I=1,NMR)
      WRITE(6,100) (A(I), I=1,NMR)
      DO 5 J=1,NMR
 5    VY(NE,J) = VY(NE,J) + A(J)
      RETURN
 100  FORMAT(/10X,7(1PE10.3,2X))
 101  FORMAT(/1 X,*ERROR ESTIMATE DUE TO ANALYSES*,/10X,7(A6,6X))
 102   FORMAT(/10X,*ERROR ESTIMATE DUE TO INITIAL VALUES*,/10X,7(A6,6X))
 103  FORMAT(/10X,*ERROR ESTIMATE DUE TO PARAMETER ESTIMATES*,/10X,7(A6,
     A6X))
      END
```

VI.4 ADDITIONAL SUBROUTINES IN CHEMIST

It was found necessary to add four subroutines to the thirty-nine programs initially present in the CHEMIST software package. These programs which are listed here are:

(i) CORR (calculates the ionic activity coefficients),
(ii) MWCALC (calculates molecular weights and charges of species,
(iii) MOLAR (calculates the molar concentrations of species),
(iv) PHSLV (calculates the acid or base needed for a specified equilibrium pH).

SUBROUTINES ADDED TO CHEMIST

```
C THIS SUBROUTINE CALCULATES THE IONIC ACTIVITY COEFFICIENTS FROM THE   COR00020
C DAVIES EQUATION( SEE DAVIES, 'ION ASSOCIATION, BUTTERWORTH, P41)       COR00030
      SUBROUTINE CORR(NAME,OP,LIT)                                      COR00010
C MWW MOLECULAR WEIGHT OF THE SOLVENT                                   COR00040
C OP PRINT CONTROL PRINTOUT IF GREATER THAN 0                           COR00050
C LIT LIMIT ON THE NUMBER OF ITERATIONS                                 COR00060
C Z1 ARRAY CONTIINING THE IONIC CHARGE OF THE COMPONENTS                COR00070
C Z ARRAY CONTAINING THE IONIC CHARGE OF THE SPECIES                    COR00080
C     A1,A2, EMPERICAL CONSTANTS IN THE DAVIES EQUATION                 COR00090
C  DENSP DENSITY OF THE PURE SOLVENT                                    COR00095
      DIMENSION PC(170),ACM(170)                                        COR00100
      REAL   KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS                        COR00110
      COMMON AIJ(460), IROW(460), JCOL(460)                             COR00120
      REAL AIJ,NAME,MWW                                                 COR00130
      COMMON /HOL8/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK, COR00140
     1   H2O,HPLUS                                                      COR00150
      COMMON /REAL8/ BBB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,    COR00160
     1   XSTART,BARMIN,SLACKS,ALITER,RT,B(60),PIE(75),V1(75),V2(75),    COR00170
     2   V3(75),V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170),  COR001[illegible]
     3   XBAR(25),R(75,75),FE,FE2,ENMB,XEMB,ENMA,XEMA                   COR00180
      COMMON /INTGR/ M,MEND,NCOMP,N,NIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,COR00190
     1  KE,MAXM,MAXP,MAXN,MAXMD,NCYCLE,NBSTAR,KPF,                      COR00200
     2   NAIJ,MAXAIJ,IOPT,NTOG,MARITH,NC(26),JCOMP(170),NEMB,NEMA       COR00210
      EQUIVALENCE (N,NTOT)                                              COR00220
      INTEGER PF                                                        COR00230
      COMMON /TOGL/ IARITH,IFIND,INTITL,INSOLV,IOUHM,ILP,IMATRX,IPUSH,  COR00240
     1               IROWS,ISCALE                                       COR00250
      COMMON/MOLER/CMW(60),Z1(60),DENSP,DENS,MWW,SMW(170),Z(170),       COR00260
     1TOT,ISTOP,K,JI,JT,A1,A2,AC(170)                                   COR00270
      IIII = 0                                                          COR00280
      DO 6 J = 1,N                                                      COR00281
      ACM(J) = 1.                                                       COR00282
C STORE THE ORIGINAL FREE ENERGY VALUES IN ARRAY PC                     COR00283
 6    PC(J) = C(J)                                                      COR00284
      MWC = 0                                                           COR00285
 7    CALL MOLAR(NAME,0.0,MWC)                                          COR00290
      SUM = 0.0                                                         COR00300
      DO 1 J = JI,JT                                                    COR00310
C CALCULATE IONIC STRENGTH                                              COR00320
 1    SUM = SUM + X1(J)*Z(J)*Z(J)                                       COR00330
      SUM = 0.50*SUM                                                    COR00340
      T1 = SQRT(SUM)                                                    COR00350
C CALCULATE THE IONIC STRENGTH FACTOR                                   COR00370
      T2 = (T1/(1.0 + T1) - A2*SUM)                                     COR00380
      KTRAC = 1                                                         COR00390
      DO 2 J = JI,JT                                                    COR00400
      AC(J) = 0.00
      AC(J) = -(Z(J)*Z(J)*A1*T2)                                        COR00410
```

```
      AC(J) = 10.0**AC(J)                                               COR00420
      DIFF = ABS(ACM(J)-AC(J))                                          COR00430
    2 IF(DIFF.GT.0.013) KTRAC = 2                                       COR00440
      GO TO (8,12),KTRAC                                                COR00450
   12 DO 3 J = JI,JT                                                    COR00460
      ACM(J) = AC(J)                                                    COR00470
C CONVERT THE A3TIVITY COEFFICIENTS FROM MOLAR TO MOLE FRACTION SCALE   COR00536
      AC(J) = (AC(J)*DENS*MWW*XBAR(K))/(TOT*DENSP)                      COR00537
    3 C(J) = PC(J) + ALOG(AC(J))                                        COR00540
      CALL SOLVE                                                        COR00545
      MARITH = 1                                                        COR00550
      IF(PF.GT.-1) CALL ERRORS                                          COR00560
      IF(IERROR.NE.1) GO TO 11                                          COR00700
      IF(IIII.GT.LIII) GO TO 8                                          COR00770
      IIII = IIII + 1                                                   COR00780
      GO TO 7                                                           COR00800
    8 IF(OP.LE.0.0) GO TO 11                                            COR00810
      WRITE(NOT,104) NAME                                               COR00820
  104 FORMAT(/1 X,'LISTING OF THE FINAL CONCENTRATION IN COMPARTMENT ',ACOR00830
     16,/10X,'SPECIES',8X,'NO. OF MOLES',3X,'MOLE FRACTION',2X,'MOLAR COCOR00840
     2NCENTRATION',2X,'LOG - MOLE     ACTIVITY COEFFICIENTS')
      DO 9 J = JI,JT                                                    COR00860
    9 WRITE(NOT,105) KN(J),X(J),XMF(J),X1(J),X2(J),AC(J)                COR0087
   11 IF(PF.GT.-1) WRITE(NOT,106) SUM                                   COR00880
      DO 10 J = JI,JT                                                   COR00890
   10 C(J) = PC(J)                                                      COR00900
  105 FORMAT(/1 X,A8,9X,1PE12.4,3X,1PE12.4,4X,E12.5,6X,0P,F9.5,7X,F10.5)COR00910
  106 FORMAT(/10X,'THE FINAL IONIC STRENGTH WAS ',1PE12.4,'MOLES/LITER')COR00920
      RETURN                                                            COR00930
      END                                                               COR00940
C SUBQUTINE CAL3ULATES THE MOLAR CONCENTRATION
      SUBROUTINE MOLAR(NAME,OPP,MWC)                                    MOL00010
C NAME NAME OF THE COMPARTMENT                                          MOL00020
C TOT SUM OF THE WEIGHTS OF THE SOLUTES (GRAMS)                         MOL00030
C - OP PRINT CONTROL IF GREATER THAN 0 PRINTOUT                         MOL00040
C - MWC IF GREATER THAN ZERO THEN MOLECULAR WEIGHTS HAVE BEEN CALCULATEDMOL00050
C - DENS AVERAGE DENSITY OF THE SOLUTION AT SYSTEM TEMPERATURE          MOL00060
C - THIS SUBROUTINE CALCULATES THE MOLAR CONCENTRATIONS                 MOL00070
      REAL   KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS                        MOL00080
      COMMON AIJ(460), IROW(460), JCOL(460)                             MOL00090
      REAL AIJ,NAME,MWW                                                 MOL00100
      COMMON /HOL8/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK, MOL00110
     1  H2O,HPLUS                                                       MOL00120
      COMMON /REAL8/ BBB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,    MOL00130
     1   XSTART,BARMIN,SLACKS,ALITER,NT,B(60),PFE(75),V1(75),V2(75),    MOL00140
     2   V3(75),V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170),  MOL00150
     3   XBAR(25),R(75,75),FE,FE2,ERMB,XEMB,ERMA,XEMA                   MOL00170
      COMMON /INTGR/ M,MEND,NCOMP,N,NIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,MOL00180
     1   KE,MAXM,MAXP,MAXN,MAXMD,NCYCLE,NBSTAR,NPF,                     MOL00190
     2   NAIJ,MAXAIJ,IOPT,MTOG,MARITH,NL(26),JCOMP(170),NEMB,NEMA       MOL0200
      EQUIVALENCE (N,NTOT)                                              MOL00210
      INTEGER PF                                                        MOL00220
      COMMON /TOGL/ IARITH,IFIND,INTITL,INSOLV,IJOHN,ILP,IMATRX,IPUSH,  MOL00230
     1               IROWS,ISCALE                                       MOL00240
      COMMON/MOLER/CMW(60),Z1(60),DENSP,DENS,MWW,SMW(170),Z(170),       MOL00250
     1TOT,ISTOP,K,JI,JT,A1,A2,AC(170)                                   MOL00260
      IF(MWC.LE.0) CALL MWCALC(NAME,0.0,MWC)                            MOL00270
```

```
      IF(ISTOP.GT.1) CALL EXIT
      IF(K.GT.NCOMP) CALL EXIT
C MOLAR CONCENTRATIONS ARE STORED IN THE X1 ARRAY
      CALL BAR(X,XBAR)
      TOT = 0.000
      T1 = 1000.0*DENS
      DO 1 J = JI,JT
      XMF(J) = X(J)/XBAR(K)
    1 TOT = TOT + X(J)*SMW(J)
      DO 2 J = JI,JT
      X1(J) = (T1*X(J))/TOT
    2 X2(J) = ALOG10(X1(J))
      IF(OPP.LE.0.000) GO TO 3
      WRITE(NOT,100) NAME
      DO 4 J = JI,JT
    4 WRITE(NOT,101) KN(J),J,XMF(J),X1(J),X2(J)
  100 FORMAT(/10X,'LISTING OF THE MOLAR CONCENTRATIONS OF SPECIES IN COM
     1PARTMENT ',A6,/10X,'SPECIES NAME',8X,'SPECIES NO.',9X,'MOLE FRACTI
     2ON',7X,'MOLAR CONCENTRATION',7X,'LOG-MOLE')
  101 FORMAT(/1 X,A6,I4X,I5,15X,1PE12.4,8X,1PE12.4,16X,0PF10.5)
    3 RETURN
      END
C  SUBROUTINE CALCULATES THE MWCALC WEIGHT AND CHARGE OF SPECIES
      SUBROUTINE MWCALC(NAME,PP,MWC)
C SMW SPECIES MOLECULAR WEIGHTS
C CMW COMPONENT MOLECULAR WEIGHTS
C NAME COMPARTMENT NAME
C THIS SUBROUTINE CALCULATES THE MOLECULAR WEIGHTS FOR MOLAR
C      INTEGER END,BLANK,H2O,HPLUS
      REAL    KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS
      COMMON AIJ(460), IROW(460), JCOL(460)
      REAL AIJ,NAME,MAW
      COMMON /HOL8/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK,
     1    H2O,HPLUS
      COMMON /REAL8/ BBB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,
     1    XSTART,BARMIN,SLACKS,ALITER,KT,B(60),PIE(75),V1(75),V2(75),
     2    V3(75)=V4(75),X(170),XMF(170),C(170),X1(170),X2(170),X3(170),
     3    XBAR(25),R(75,75),FE,FE2,ERMB,XEMB,ERMA,XEMA
      COMMON /INTGR/ M,MEND,NCOMP,NINIT,NOT,PF,ITER,ITMAX,IERROR,LASTCP,
     1    KE,MAXM,MAXP,MAAN,MAAMD,NCYCLE,NBSTAR,NPF,
     2    NAIJ,MAXAIJ,IOPT,MTOG,MARITH,KL(26),JCOMP(170),NEMB,NEMA
      EQUIVALENCE (N,NJOT)
      INTEGER PF
      COMMON /TOGL/ IARITH,IFIND,INTITL,INSOLV,IJOHN,ILP,IMATRX,IPUSH,
     1               IROWS,ISCALE
      COMMON/MOLER/CMW(60),Z1(60),DENSP,DENS,MAW,SMW(170),Z(170),
     1TOT,ISTOP,K,JI,JT,A1,A2,AC(170)
C TEST FOR MOLECULAR WEIGHT DATA
      ISTOP = 0
      DO 1 I = 1,M
      IF(CMW(I)) 2,2,1
    2 WRITE(NOT,98) I,NR(I,1)
   98 FORMAT(/5X,'NO MOLECULAR WEIGHT DATA FOR ROW',I5,' CALLED ',A6)
      ISTOP = 2
    1 CONTINUE
      IF(ISTOP.GT.1) GO TO 3
C FIND THE COMPARTMENT NUMBER
```

```
      CALL LOOKUP(NAME,K,1,NCOMP,NAM)                                   MWC00350
C FIND THE RANGE OF SPECIES' NO.'S IN THE COMPARTMENT                    MWC00360
      IF(K.GT. NCOMP) GO TO 6                                           MWC00370
      JI = KL(K)                                                        MWC00380
      IF(K.EQ.NCOMP) JT = NTOT                                          MWC00390
      IF(K.LT.NCOMP) JT = KL(K+1) -1                                    MWC00400
      DO 4 J = JI,JT                                                    MWC00410
      CALL FIND(0,J,IJLOC,IFLAG)                                        MWC00420
      IF(IJLOC.EQ.0) GO TO 4                                            MWC00430
      SMW(J) = 0.0000                                                   MWC00440
      Z(J) = 0.000000000                                                MWC00445
      DO 5 JJ = IJLOC,IFLAG                                             MWC00450
      II = IROW(JJ)                                                     MWC00455
      SMW(J) = SMW(J) + AIJ(JJ)*CMW(II)                                 MWC00460
      Z(J) = Z(J) + AIJ(JJ)*Z1(II)                                      MWC00465
 5    CONTINUE                                                          MWC00468
 4    CONTINUE                                                          MWC00470
      IF(PP.LE.0.000) GO TO 3                                           MWC00480
      WRITE(NOT,100) NAME                                               MWC00490
 100  FORMAT(/10X,'LISTING OF THE MOLECULAR WEIGHTS OF THE SPECIES IN COMWC00500
     1MPARTMENT  ',A10)                                                 MWC00510
      WRITE(6,200)
      DO 55 J = JI,JT
 55   WRITE(6,201) KN(J),J,Z(J),SMW(J)
 200  FORMAT(//10X,'SPECIES - NO.',4X,'CHARGE',4X,'MOLECULAR WEIGHT')
 201  FORMAT(/10X,A6,3X,I3,4X,F8.4,4X,F12.4)
      MWC = 1                                                           MWC00475
      GO TO 3                                                           MWC00565
 6    WRITE(NOT,99) NAME                                                MWC00570
 99   FORMAT(/9X,'THERE IS NO COMPARTMENT NAMED ',A6,/10X,'RETURN FROM  MWC00580
     1MWCALC')
 3    RETURN                                                            MWC00600
      END
      SUBROUTINE PHSLV(NAME,VALUE,LIM,IC)                               PHSL0010
C SUBROUTINE CALCULATES THE INCREMENT OF ACID REQUIRED TO OBTAIN THE    PHSL0020
C DESIRED PH VALUE                                                      PHSL0030
C NAME IS THE COMPARTMENT ON WHICH THE PH ADJUSTMENT IS MADE            PHSL0040
C VALUE IS THE DESIRED PH VALUE                                         PHSL0050
C LIM IS THE NUMBER OF ITERATIONS POSSIBLE IN ONE SEARCH                PHSL0055
C IC IF IC = 2 IONIC ACTIVITY CORRECTIONS ARE MADE                      PHSL0052
C IC IF IC = 1 PROBLEM IS SOLVED IN TERMS OF CONCENTRATIONS             PHSL0054
C CL- IS THE COUNTERION ASSOCIATED WITH THE PROTON                      PHSL0060
C OH- IS THE HYDROXIDE ION NAME                                         PHSL0062
C NA+ IS THE COUNTERION ASSOCIATED WITH THE HYDROXIDE ION               PHSL0064
C WRITTEN BY P B MELNYK FEB. 1972                                       PHSL0070
C                                                                       PHSL0075
      REAL    KA,KB,NR,KN,NAM,END,BLANK,H2O,HPLUS                       PHSL0080
      COMMON AIJ(460), IROW(460), JCOL(460)                             PHSL0090
      REAL AIJ                                                          PHSL0100
      COMMON /HOL8/ KA(12),KB(12),NR(60,2),KN(170),NAM(25,2),END,BLANK, PHSL0110
     1   H2O,HPLUS                                                      PHSL0120
      COMMON /REAL8/ BBB(60,5),PH(25),T(20),BMULT(5),TOL1,TOL2,XMIN,    PHSL0130
     1   XSTART,BARMIN,SLACKS,ALITER,RT,B(60),PIE(75),V1(75),V2(75),    PHSL0140
     2   V3(75)IV4(75),X(170),AMF(170),C(170),X1(170),X2(170),X3(170),  PHSL0150
     3   XBAR(25),R(75,75),FE,FE2,ERMB,XEMB,ERMA,XEMA                   PHSL0160
      COMMON /INTGR/ M,MEND,NCOMP,N,NIT,NOT,PP,ITER,ITMAX,IERROR,LASTCP,PHSL0170
     1   KE,MAXM,MAXP,MAXN,MAXND,NCYCLE,NBSTAR,NPP,                     PHSL0180
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     2    NAIJ,MAXAIJ,ICPT,MTOG,MARITH,KL(26),JCOMP(170),NEMB,NEMA         PHSL0190
      EQUIVALENCE (N,NTOT)                                                PHSL0200
      INTEGER PF                                                          PHSL0210
      COMMON /TOGL/ IARITH,IFIND,INITIL,INSOLV,IJOHN,ILP,IMATRX,IPUSH,    PHSL0220
     1              IROWS,ISCALE                                          PHSL0230
      REAL NAME,NAPOS                                                     PHSL0232
      DATA CLNEG,NAPOS,OHNEG/6HCL-    ,6HNA+    ,6HOH-    /               PHSL0234
C                                                                         PHSL0240
C FIND THE COMPARTMENT                                                    PHSL0250
      DO 1 K = 1,NCOMP                                                    PHSL0260
      IF(NAME.EQ.NAM(K,1))GO TO 2                                         PHSL0270
    1 CONTINUE                                                            PHSL0280
      WRITE(NOT,99) NAME                                                  PHSL0290
   99 FORMAT(5X,16H NO COMPARTMENT ,A6)                                   PHSL0300
      CALL EXIT                                                           PHSL0310
    2 NHPLUS = 0                                                          PHSL0320
      NCL = 0                                                             PHSL0330
      NNA = 0                                                             PHSL0331
      NOH = 0                                                             PHSL0332
      KK = K                                                              PHSL0335
      DO 5 I = 1,M                                                        PHSL0340
      IF(HPLUS.EQ.NR(I,1))NHPLUS = I                                      PHSL0350
      IF(CLNEG.EQ.NR(I,1)) NCL = I                                        PHSL0360
      IF(NAPOS.EQ.NR(I,1)) NNA = I                                        PHSL0362
      IF(OHNEG.EQ.NR(I,1)) NOH = I                                        PHSL0364
    5 CONTINUE                                                            PHSL0370
      ITR = 0                                                             PHSL0380
      PHNOW = PHCALC(KK)                                                  PHSL0408
   14 DIFF = VALUE-PHNOW                                                  PHSL0410
      IF(DIFF) 10,11,12                                                   PHSL0420
C     ADD ACID                                                            PHSL0430
   10 IF(ABS(DIFF).LE.2.0E-02)  GO TO 11                                  PHSL0440
      MARITH = 0                                                          PHSL0444
      MS1 = 1                                                             PHSL0446
      CALL ARITH                                                          PHSL0450
      IF(KE.NE.0) RETURN                                                  PHSL0460
      RATE = 0.000                                                        PHSL0470
      RATE1 = PART(-1,-KK,2,0,NHPLUS)                                     PHSL0480
      RATE2 = PART(-1,-KK,2,0,NCL)                                        PHSL0490
      WRITE(NOT,92) RATE1,RATE2                                           PHSL0500
   92 FORMAT(//5X,'THE PARTIAL DERIVATIVES',5X,'H+',1PE12.4,5X,'CL-',1PEPHSL0510
     112.4)                                                               PHSL0520
      RATE = RATE1 + RATE2                                                PHSL0530
      FAC = DIFF/RATE                                                     PHSL0535
      BMULT(5) = BMULT(5) + FAC                                           PHSL0540
      GO TO 13                                                            PHSL0550
C ADD BASE                                                                PHSL0555
   12 IF(ABS(DIFF).LE.1.000E-03) GO TO 11                                 PHSL0560
      MS1 = -1                                                            PHSL0564
      MARITH = 0                                                          PHSL0566
      CALL ARITH                                                          PHSL0570
      IF(KE.NE.0) GO TO 11                                                PHSL0580
      RATE = 0.000                                                        PHSL0590
      RATE1 = PART(-1,-KK,2,0,NOH)                                        PHSL0600
      RATE2 = PART(-1,-KK,2,0,NNA)                                        PHSL0610
      RATE = RATE1 + RATE2                                                PHSL0620
      WRITE(NOT,94) RATE1,RATE2                                           PHSL0630
```

```
 94   FORMAT(//5X,'THE PARTIAL DERIVATIVES',5X,'OH-',1PE12.4,5X,'NA+',1PPHSL0640
     1E12.4)
      FAC = DIFF/RATE                                                   PHSL0650
      BMULT(4) = BMULT(4) + FAC                                         PHSL0655
 13   CALL ROWS(-1)                                                     PHSL0660
      IF(PF.GT.-1) CALL ROWS(-2)                                        PHSL0670
      IF(IC.EQ.1) CALL SOLVE                                            PHSL0680
      IF(IC.EQ.2) CALL CORR(NAME,0.0,LIM)                               PHSL0690
      IF(IERROR.NE.1) GO TO 11                                          PHSL0695
      ITR = ITR + 1                                                     PHSL0700
      PHNOW = PHCALC(KK)                                                PHSL0710
      WRITE(NOT,93) NAM(KK,1),PHNOW                                     PHSL0720
      IF(ITR.GT.LIM) GO TO 20                                           PHSL0721
      D1 = VALUE + .01                                                  PHSL0722
      D2 = VALUE - .01                                                  PHSL0724
      IF((MS1.EQ.-1).AND.(PHNOW.GT.D1)) GO TO 15                        PHSL0726
      IF((MS1.EQ.+1).AND.(PHNOW.LT.D2)) GO TO 15                        PHSL0728
 93   FORMAT(//5X,'THE PH VALUE FOR COMPARTMENT ',A6,' IS ',1PE12.4)    PHSL0730
      IF(ITR.LE.LIM) GO TO 14                                           PHSL0740
 20   DIFF = VALUE -PHNOW                                               PHSL0750
      WRITE(NOT,91) DIFF                                                PHSL0760
 91   FORMAT(5X,16H ERROR IN PH IS ,1PE12.4)                            PHSL0770
 11   RETURN                                                            PHSL0780
 15   IF(MS1) 16,16,17                                                  PHSL0790
 16   BMULT(4) = BMULT(4) - FAC                                         PHSL0800
      FAC = FAC*0.5                                                     PHSL0810
      BMULT(4) = BMULT(4) + FAC                                         PHSL0820
      WRITE(NOT,95)                                                     PHSL0830
 95   FORMAT(/5X,'THE STEPSIZE HAS BEEN REDUCED BY ONE HALF ')          PHSL0840
      GO TO 13                                                          PHSL0850
 17   BMULT(5) = BMULT(5) -FAC                                          PHSL0860
      FAC = FAC*0.5                                                     PHSL0870
      WRITE(NOT,95)                                                     PHSL0880
      BMULT(5) = BMULT(5) + FAC                                         PHSL0890
      GO TO 13                                                          PHSL0900
      END                                                               PHSL0910
                                                                        PHSL0910
```

VI.5 RATE EXPRESSIONS: POLYPHOSPHATE HYDROLYSIS

Three function statements which are used to calculate the tripoly-, pyro-, and ortho-phosphate concentrations at specified time intervals are listed here. In each function statement, the integrals of the zero and first order reaction rate expressions are programmed. These programs were used with the Simplex program to estimate the first order rate constants of polyphosphate hydrolysis as described in Chapter IV, Section 5.

```
C                                 POLYPHOSPHATE HYDROLYSIS
C  FUNCTION STATEMENT TO CALCULATE THE TRIPOLYPHOSPHATE CONCENTRATION AFTER
C  HYDROLYSIS
      FUNCTION POLY(NR,TIME)
C NR ORDER OF REACTION RATE
C  TIME TIME AT WHICH PHOSPHATE CONCENTRATION IS TO BE ESTIMATED
      COMMON CZO(2),CFO(2),POLYI,PYROI,ORTHOI
      IF(NR)1,1,2
C ZERO ORDER REA3TION RATE
 1    POLY = POLYI-CZO(1)*TIME
      IF(POLY.LT.0.) POLY = 0.
      RETURN
C FIRST ORDER REACTION RATE
 2    POLY = POLYI*EXP(-CFO(1)*TIME)
      RETURN
      END
C  FUNCTION STATEMENT TO CALCULATE PYROPHOSPHATE CONCENTRATION AFTER HYDROLYS
      FUNCTION PYRO(NR,TIME)
C NR ORDER OF REACTION RATE
C  TIME TIME AT WHICH PHOSPHATE CONCENTRATION IS TO BE ESTIMATED
      COMMON CZO(2),CFO(2),POLYI,PYROI,ORTHOI
      IF(NR) 1,1,2
C ZERO ORDER REACTION RATE
 1    A = POLYI/CZO(1)
      IF(TIME-A) 3,4,4
 3    PYRO = PYROI + (CZO(1) -CZO(2))*TIME
      IF(PYRO.LT.0.) PYRO = 0.
      RETURN
 4    PYRO = PYROI + (1.-CZO(2)/CZO(1))*POLYI - CZO(2)*TIME
      IF(PYRO.LT.0.) PYRO = 0.
      RETURN
C FIRST ORDER REICTION RATE
 2    B = PYROI*(CFO(2) - CFO(1))/(POLYI*CFO(1))
      B = B-1.
      C = POLYI*CFO(1)/(CFO(2)-CFO(1))
      PYRO = C*(EXP(-CFO(1)*TIME) + B*EXP(-CFO(2)*TIME))
      RETURN
      END
C  FUNCTION STATEMENT TO CALCULATE THE ORTHOPHOSPHATE CONCENTRATION AFTER
C  HYDROLYSIS
      FUNCTION ORTHO(NR,TIME)
      COMMON CZO(2),CFO(2),POLYI,PYROI,ORTHOI
      IF(NR) 1,1,2
C NR ORDER OF REACTION RATE
C  TIME TIME AT WHICH PHOSPHATE CONCENTRATION IS TO BE ESTIMATED
C ZERO ORDER REACTION RATE
 1    TC = POLYI/CZO(1)
```

```
      IF(TIME-TC) 3,4,4
 3    ORTHO = ORTHOI + (CZO(1) + 2.*CZO(2))*TIME
      IF(ORTHO.LT.0.) ORTHO = 0.
      RETURN
 4    ORTHO = ORTHOI + ((CZO(1) + 2.*CZO(2))/CZO(1))*POLYI + 2.*CZO(2)*T
     1IME
      IF(ORTHO.LT.0.) ORTHO =0.
      RETURN
C FIRST ORDER REACTION RATE
 2    A = PYROI*(CFO(2)-CFO(1))/(POLYI*CFO(1))
      A = A-1.
      B = CFO(2)*EXP(-CFO(1)*TIME) + A*CFO(1)*EXP(-CFO(2)*TIME)
      C = CFO(2) + A*CFO(1)
      D = 2./(CFO(2)-CFO(1))
      ORTHO =-POLYI*(EXP(-CFO(1)*TIME) + D*B) + POLYI*(1. + D*C) +
     1ORTHOI
      RETURN
      END
```