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ANALYSIS OF THE OPTIMUM EXTRACTION SYSTEM DESIGN FOR THE SEPARATION AND PURIFICATION OF RARE EARTHS

by
Kenneth Yeon-Kang Chan

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Analysis of the
Optimum Extraction System Design
for the Separation and Purification
of Rare Earths

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ABSTRACT

Analysis of the
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A mathematical model for the liquid-liquid equilibrium of the lanthanide and yttrium oxides in the nitric acid - water - tributyl phosphate (HNO_3-H_2O-TBP) two-phase system has been developed. This model is based on the inter-relationships of chemical reactions, phase equilibrium, and material balance. The chemical reactions were modelled using experimentally derived empirical equations for components involved. The distribution coefficients of 16 rare earths which were experimentally determined by UK Harwell Laboratory were used to evaluate the parameters of this equilibrium model. Once model parameters are determined, material balance for all species in the HNO_3-H_2O-TBP two-phase system can be accomplished simultaneously.

The developed equilibrium model was validated by a published experimental extraction system for the separation and purification of specific component from the mixture of lanthanide and yttrium elements.

This model was used for analyzing the minimum production cost of extraction systems for (1) separation and purification of europium from the lanthanide and yttrium mineral sample; and (2) purification of yttrium from the mixture of lutetium, ytterbium and yttrium.

This thesis is dedicated to my parents
Shu-Chien and Chiming Chan

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The rare earth elements of lanthanide and yttrium are important and essential raw materials for various industries. Currently, they are widely used in metallurgy, glass, ceramics, illumination, electronics, chemicals, magnets and nuclear areas. The largest use of rare earths is as catalysts in petroleum operations. However, specific rare earth elements are rapidly gaining importance as ingredients in many new applications. These include glass and ceramics, lasers, communication and computer systems, color television, and microwave. The demand for specific rare earths - yttrium, scandium, neodymium, samarium, lanthanum, cerium, and dysprosium - is expected to increase rapidly. This is due to their potential use in high technology applications such as high-intensity magnets, laser, and superconductor materials.

Due to their similar atomic structures and chemical properties, the separation of rare earths into individual elemental compounds is difficult. Because of technical and economic limitations, liquid-liquid extraction has emerged in recent years as a major separation process for rare earths. In a typical rare earths processing plant, over one hundred contact stages are being used in order to have them separated and purified, and meet the purity specifications (sometimes up to 99.99%).

1.2 Development Of The Rare Earths Equilibrium Model

Tri-n-butyl Phosphate (TBP) has many desirable solvent characteristics in extracting rare earth nitrate from aqueous solution: its relatively high distribution coefficients and separation factors, low volatility, and immiscibility with water when pre-equilibrated with it. Therefore, many attempts and efforts have been done since the early fifties, in exploring the applicabilities of rare earths separation and purification, in developing a model for predicting the rare earths distribution in two immiscible phases, and in developing a method for foretelling the stage-wise process conditions in an liquid-liquid extraction operation (3).

This early research work was conducted by the Ames Laboratory of the Atomic Energy Commission, at Ames, Iowa. Bochinski and his colleagues (1) laid the groundwork by developing a method for stage-wise calculations from the equilibrium constants and separation factor data in an extraction operation. Knapp and co-workers (2) obtained equilibrium constants and separation factor data for various rare earth mixtures both in acidic and neutral organophosphorus extractant systems. Schoenherr (3) developed a method of predicting equilibria for certain rare earth nitrates in the HNO_3-H_2O-TBP system. By observing the distribution of neodymium nitrate - nitric acid mixtures, he found that the distribution of neodymium nitrate was approximately the same as that of nitric acid. This phenomenon was also observed for the distribution of mixtures of samarium nitrate and nitric acid. Thus the conclusion was drawn that the distribution of nitric acid alone could be used as a good approximation of the distributions of neodymium nitrate - nitric acid mixtures and samarium nitrate and nitric acid.

A Russian group made an extensive practical study of extraction of rare earths by TBP from nitrate solutions. Pebalk et al. (4) derived equations from equilibrium curves, so they could calculate the number of theoretical stages required for a specific degree of separation of rare earth elements by TBP extraction.

Some semiempirical models were also developed by Eills (5) and Ioannou et al. (6). Their theories are based on the similarity between gas adsorption or vapor-liquid equilibrium and extraction equilibrium. Models like this have greater applicability than others to hydrometallurgical systems.

Hoh and Bautista (7), presented a method for the prediction of distribution coefficients in the Pu(IV) and Np(IV) nitrate-HNO_3-TBP(dilute) systems, based on the thermodynamic equations for extraction of the species using chemically based models. The predictive model equation makes use of the aqueous actinide nitrate complex stoichiometric stability constant expressed as degree of formation, the extraction mechanism derived by them, and the equilibrium constant for the extraction reaction. Good agreements were obtained between the reported experimental data and the predicted values. Later on, Hoh and Bautista (8) expanded their model from binary system to multicomponent systems. The theory for multicomponent was based on the assumption that the activity coefficient varies only slightly with its concentration. The experimental results show that the data fit the binary model very well and to a lesser degree the ternary model. The variance between the experimental data and the ternary models is attributed to the omission of the interaction terms between species.

Recently, Horng (9), Horng and Maa (10) developed a semiempirical model for the extraction of metals in acid media by neutral, acidic and basic solvent, based on reaction kinetics. After extensively studying the extraction kinetics for the metal using these three types of extractants, they assumed that the extraction rate of metallic species is pseudo first order with respect to its concentration and the concentration of organic extractant. The stripping rate of metallic species in the organic phase is also pseudo first order with respect to its concentration. Based on the assumptions they made, generalized expressions for the reaction kinetic were developed. The parameters of expressions were evaluated by fitting the expressions to the experimental equilibrium data from 60 different systems. A non-linear optimization method was applied. The model has been tested in the $UO_2(NO_3)_2$-HNO_3-TBP system. The agreement between the experimental and predicted distribution data is very satisfactory except at low aqueous acidity.

1.3 The Scope Of This Research

The scope of this research has been in development of a mathematical model for predicting the distribution coefficients of rare earth in the HNO_3-H_2O-TBP two-phase system, with large acidity range in the aqueous phase. Theoretically, this model is based on the inter-relationships of chemical reactions, phase equilibrium, material balance, activity coefficients, and empirical equations for the concentration of chemical species which are involved in the extraction mechanism. Because of the engineering point of view, this research is more focus on the **fact** than the **theory**. Multistage liquid-liquid extraction equipment is operated frequently in an adiabatic manner. When entering streams are at the same temperature and heat of mixing is negligible, the operation is also isothermal. Therefore, no relationship in heat or temperature is involved in this model, even though the temperature will affect the distribution coefficients (68). Practical process design of separation and purification of rare earths are also part of this research. Finally the analysis of the optimum extraction system design in terms of capital costs and operating costs for the separation and purification of rare earths concludes this research.

Chapter 2 lays the theoretical foundation of this chemical based, semiempirical distribution coefficient model. Literatures, chemistry, theories, definitions, experimental data, and all necessary information involving the model construction are briefly discussed in this chapter.

Chapter 3 discusses the construction of the model. The expression of distribution model was derived in terms of activities, together with the development of other accessories relationships.

Chapter 4 discusses the evaluation of model parameters. A non-linear optimization technique is applied. The deviation of the model predicted data and the actual experimental data is treated as the object function in the optimization algorithm. The formulas or equations for the inter-relationships are used as equality constraints, and all specie concentrations and parameters as inequality constraints, because they all greater than zero and less than a positive finite number.

This model has been verified using published data with satisfactory results. The experiments of separating the promethium from mixed fission product rare earths by extraction were used to verify the accuracy of this model. By comparing the laboratory reported with model predicted operating conditions, we have concluded that this model accurately predicts liquid-liquid equilibrium. All discussions of model verification are included in Chapter 5. A computer program was developed to simulate the liquid-liquid extraction operations.

Chapter 6 discuss the separation and purification of europium from a rare earths mineral sample taken from Jiangxi Province, China. The composition of the Jiangxi sample includes all 15 rare earth elements except promethium, because promethium does not exists in natural rocks. The effects of the number of stages on europium extraction were studied extensively in the HNO_3-H_2O-TBP system. The conclusion drawn from the europium purification is that the recovery and purity of product are governed by the acidity of the aqueous solution, ratio of aqueous solution rate to the organic extractant rate, and the number of contact stages. Similar discussions for yttrium purification processes are included in Chapter 7.

All economic aspects are included in Chapter 8. The total production cost consists of capital investment and operating costs. The capital investment was estimated by directly relates the total capital cost to the expenses for purchased equipment by a multiplying factor. The operating costs include: costs for raw materials, replacing of loss solvent, labor and maintenance, loss incurred by unrecovered solute and interest charges. Cost analysis were made for three case studies: the separation and purification of europium oxide; the purification of yttrium oxide; and the separation of gadolinium from the sub-group Ga-La. The optimum process parameters for all cases were also given, this includes operating conditions and number of stages required, in terms of minimum total production cost.

Finally, Chapter 9 concludes this research work and some suggestions were made for further development in the future.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Distribution Coefficient

Liquid-Liquid extraction is a separation technique which is widely used both in industries and laboratories. It involves two immiscible (or partial miscible) liquid phases: a second liquid, or solvent is introduced to the original mixture or solution, to provide a second phase.

This is in contrast to direct separation techniques. For example, distillation, where heat is used to provide a vapor phase. The second liquid is chosen such that the desired component in the original mixture is extracted or preferentially transfers into the second liquid. The two liquid phases are then physically separated and the extracted component is recovered from the solvent by other separation techniques, such as distillation, precipitation, etc.

Liquid-Liquid extraction is employed for separations when it is the only method available or the most economical technique. Because the foreign substance, or solvent, is added to the separation system, a second separation step is therefore needed to recover the extracted component from the solvent. This technique is obviously only used for separations which cannot easily be achieved in a single step. It is a method which exploits chemical or structural differences between the species of the mixture rather than molecular size, and is therefore complementary to distillation (65).

When a solute is distributed between two liquid phases, the **distribution coefficient** **(K_d)** is defined as the ratio of the concentrations of the solute in each liquid phase at equilibrium:

$$K_d = \frac{Y_a}{X_a} \qquad (2.1)$$

Where Y_a = mole fraction of solute a in the extract

X_a = mole fraction of solute a in the raffinate

The distribution coefficient K_d is one of the most important parameters used in the extraction operation.

The selectivity of a solvent for solute A as against B or **separation factor (SF)** can be described by the ratio of distribution coefficients for the two components:

$$SF = \frac{K_{da}}{K_{db}} = \frac{Y_a / X_a}{Y_b / X_b} \qquad (2.2)$$

This is similar to relative volatility in distillation. When two components are to be separated by Liquid-Liquid extraction, the ratio of one component to another must be different in each of the two phases.

Most extractions of inorganic compounds involve very complex chemical reactions. For example, during the extraction of rare earth species from nitric acid solution by tri-n-butyl phosphate (TBP), $(C_4H_9O)_3PO$, reactions take place not only between the TBP and the rare earth nitrate to be extracted, but also involved are: the ionization of nitric acid, the complexes formed between the rare earth ion and nitrate in the aqueous phase; and the complexes nitrate and TBP in the organic phase. In the following discussion, the brackets [ ] represent the **activities**, the parentheses ( ) mean **concentrations**, and the subscripts **A** and O denote the **aqueous** phase and **organic** phase, respectively.

2.2 The Extraction System

Generally a liquid-liquid extraction system consists of an extraction section, scrubbing section, stripping section, and solvent washing section, if necessary (Figure 2.1). In all such operations, the solution which is to be extracted is called the feed, and the liquid with which the feed is contacted is the solvent. The solvent-rich product of the operation is called the extract, and the residual liquid from which solute has been removed is the raffinate.

If the concentration of impurities in the extract is greater than tolerance, it can be reduced by scrubbing in multistage countercurrent contact equipment. This involves contacting the extract with a second liquid phase, usually the same solvent as the original feed, which is immiscible with the extract. The composition of the scrub feed is chosen such that the desired solute is largely retained in the extract phase while the impurities are washed out. Usually, some of the desired solute is passed into the scrub liquor. To recover this lost solute, the scrub raffinate is commonly combined with the main feed stream, with the solute then being extracted in the extraction section.

After the extract leaves the scrubbing section, it is passed to a further liquid-liquid contacting section where it is equilibrated. This involves a multistage countercurrent manner with a second immiscible liquid phase, in which the solute passes to the second phase. This operation is known as stripping (or backwashing). The stripped solvent is then recycled to the extraction section, via a solvent washing operation, if necessary.

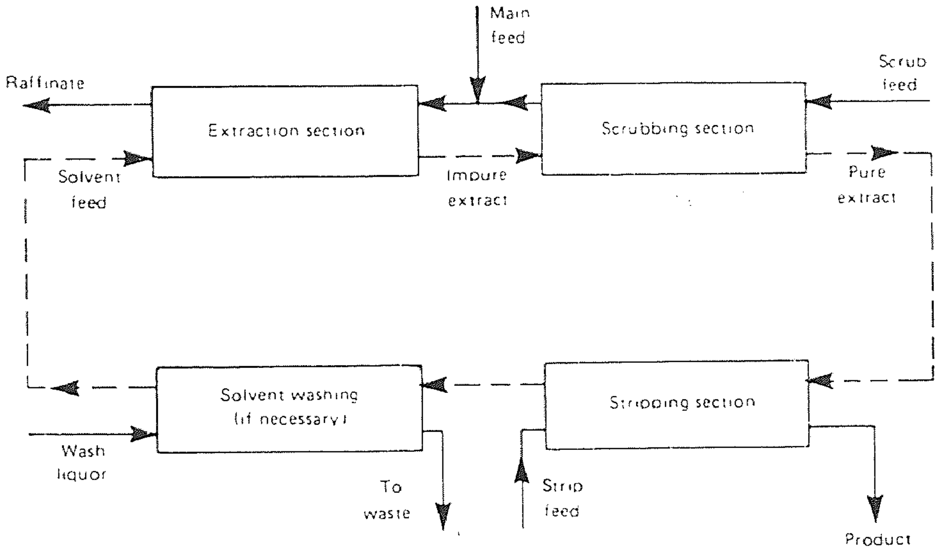

Figure 2.1 The Extraction System.

It is obvious that there is an interrelation between the stripping and extraction sections. It is not necessarily more economical to remove all the solute from the solvent in the stripping section. If we want to recover more solute from the feed, it may be less costly to use more stages or a higher solvent to feed ratio in the extraction section, than the additional stages in the stripping section to remove more solute.

2.3 Mixer Settler Extractor

Mixer-settlers have been used almost exclusively for rare earths separation (64). The mixer-settler is the simplest stagewise contactor. A mixer-settler consists of two chambers: in the first chamber, the mixer, aqueous and organic streams are continuously introduced, mixed and equilibrated; in the second chamber, the settler, the mixture overflowing from the mixer, is allowed to separate under quiescent conditions into organic and aqueous phases layers. After settling, the organic and aqueous phases are then pumped to the next stage of mixing chambers in a countercurrent manner. The basic mixer-settler is shown in Figure 2.2 Mixer-settlers are relatively easy to operate, reliable, flexible and fairly simple to design, are free of backmixing, and the stage efficiencies are usually greater than 90 per cent. With sufficient resident time and power in the mixer, and sufficient residence time in the settler, practically 100% stage efficiency can be reached (66).

A continuous multistage countercurrent mixer-settler extraction cascade is shown in Figure 2.3. Each stage will consist of a mixer and a settler. The liquids are generally pumped from one stage to the next, but gravity flow can be arranged if sufficient hydraulic head is available.

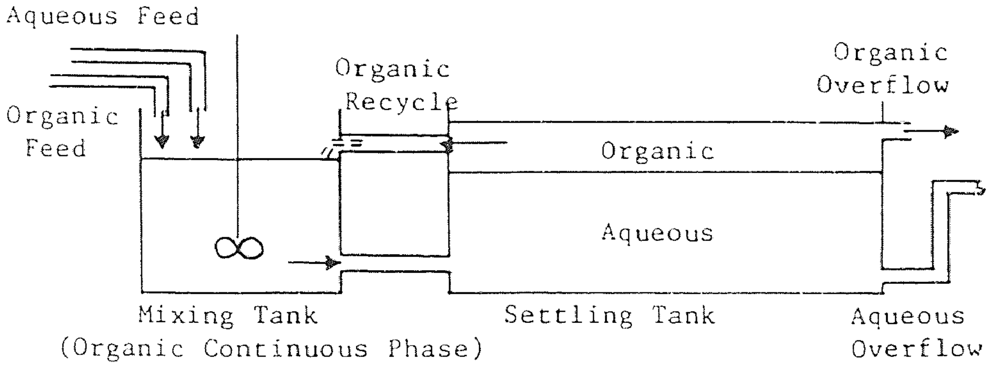

Figure 2.2 Mixer Settler Extractor.

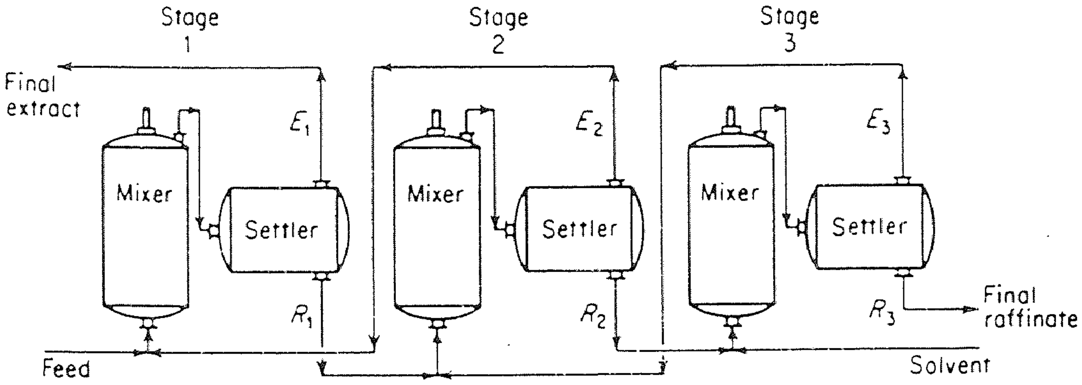

Figure 2.3 Countercurrent Mixer-settler Extraction Cascade.

2.4 Rare Earth Nitrate And TBP Complexes Formation

Most solvent extractions of inorganic compounds involve chemical reactions between the solvent and the inorganic species to be extracted. The generally accepted mechanism of rare earth oxides in nitric acid solution extracted by solvent TBP is:

$$(M^{+3})_A + 3(NO_3^{-1})_A + 3(TBP)_O = (M(NO_3)_3(TBP)_3)_O \qquad (2.3)$$

The equilibrium constant is:

$$K_e = \frac{[M(NO_3)_3(TBP)_3]_O}{[M^{+3}]_A * [NO_3^{-1}]_A^3 * [TBP]_O^3} \qquad (2.4)$$

McKay et al. (11) substantiated the existence of a grouping: a rare earth, three nitrate groups and three tributyl phosphate molecules. Hesford and co-workers (12) studied the TBP dependency of distribution ratio K_d for 9 different rare earths. They found by plotting that the log K_d vs. % TBP to be straight lines of slope 2.7-3.1. Thus, they concluded that the extracted species may be considered to be $M(NO_3)_3(TBP)_3$.

By using infra-red spectra, Bostian and Smutz (13) concluded that complexing takes place at the P=O bond on the solvent molecule; complex is formed by weak inter-molecular attractions depending on dipole effects; and therefore confirmed McKay's substantiation.

2.5 The Distribution Of Nitric Acid Between Water And TBP

Healy and McKay (14) and McKay (15) reported that nitric acid will dissolve in TBP and form the complex HNO_3-TBP. Alcock et al. (16) proposed that the reaction between nitric acid and TBP is given by the equation:

$$(H^+)_A + (NO_3^{-1})_A + (TBP)_O = (HNO_3 \cdot TBP)_O \qquad (2.5)$$

The equilibrium constant based on Alcock's experimental data is 0.16. Alcock et al. (16) postulated that all the nitric acid dissolves as $HNO_3 \cdot TBP$ breaks down, thus such compounds as $(HNO_3)_2 \cdot TBP$, $(HNO_3)_3 \cdot TBP$, etc. may also formed.

Later, Fomin and Maiorova (17) investigated the distribution of nitric acid between the aqueous phase and 1 M TBP solution in benzene. They reported the equilibrium constant of the above reaction was 0.22 with the nitric acid concentration in the initial solution up to 4 M. They assumed that the reactions between nitric acid and TBP taking place may be expressed not only by equation (2.5), but also by the equation (2.6):

$$(H^+)_A + (NO_3^{-1})_A + (HNO_3 \cdot TBP)_O = ((HNO_3)_2 \cdot TBP)_O \qquad (2.6)$$

By assuming that the equilibrium constant for equation (2.5) 0.22 is correct, Fomin and Maiorova calculated the equilibrium constant 0.002 for equation (2.6).

Sheka and Kriss (18) studied the reaction between nitric acid and TBP by means of a physicochemical analytical method using the dielectric constant as the measured property. They found that the compound $HNO_3 \cdot TBP$ predominates at nitric acid concentrations up to 4 M and $HNO_3 \cdot (TBP)_3$ is the major compound up to 9 M nitric acid concentration in the system of HNO_3-TBP-CC_4. By assuming that only the undissociated nitric acid molecules take part in the reaction, the equilibrium constants for compounds $HNO_3 \cdot TBP$ and $HNO_3 \cdot (TBP)_3$ determinated by them were 0.64 and 0.04, respectively.

Davis (19) made a series of studies on the thermodynamics of extraction of nitric acid by TBP. He postulated that compounds such as $HNO_3 \cdot TBP$, $(HNO_3)_2 \cdot TBP$, $(HNO_3)_3 \cdot TBP$ and $(HNO_3)_4 \cdot TBP$ may have formed successively, although evidence for complexes containing more than 2 moles of HNO3 per mole of TBP is very skeptical. Nikolaeva and co-workers (20) reported that the composition of complexes, obtained by the mathematical modelling method, have been confirmed by the infrared spectra. These complexes consisted of $HNO_3 \cdot (TBP)_3$, $HNO_3 \cdot (TBP)_2 \cdot (H_2O)_2$, $(HNO_3)_2 \cdot TBP \cdot (H_20)_3$, $HNO_3 \cdot TBP$, HNO_3, TBP, and H_2O. Dong and his colleagues (21) conducted the dynamic simulation for a multistage countercurrent extraction process, and reported the equilibrium constants 0.19 and 0.004 for the complexes $HNO_3 \cdot TBP$ and $(HNO_3)_2 \cdot TBP$, respectively.

From the foregoing discussion of previous research results, it is clear that many forms of the $HNO_3 \cdot TBP$ complex exist in the TBP solution (or organic phase). It is very difficult to determine precisely the concentration for each form of $HNO_3 \cdot TBP$ complex. Complete forms of the $HNO_3 \cdot TBP$ complex are still undetermined, nor are the equilibrium constants for each form available. Thus, for mathematical modelling purposes, the concept of solubility of nitric acid in the TBP solution was used.

Many discussions of solubilities of nitric acid in TBP solution are in the published literature. Experimental data can be found in Schoenheer (3), Davis (19), Healy and Brown (22), Kinney and Smutz (23), Peppard and Ferraro (24), Shuler (25), and Davis et al. (26). Based on the summarized data made by Davis and co-workers (26), Figure 2.4 illustrates the solubility of nitric acid in the TBP phase as a function of nitric acid in the aqueous phase.

A correlation of the solubility of nitric acid in the TBP phase was made based on the smoothed data presented by Davis et al. (26), so the solubility data can be built into our model.

2.6 The Solubility Of Water In The TBP Solution

Similar to HNO_3 distribution in the TBP phase, water is also found in the TBP phase in many form of complexes. Alcock and his colleagues (16) described that since $HNO_3 \cdot TBP$ actually exists partially in hydrated form, the simplest assumption

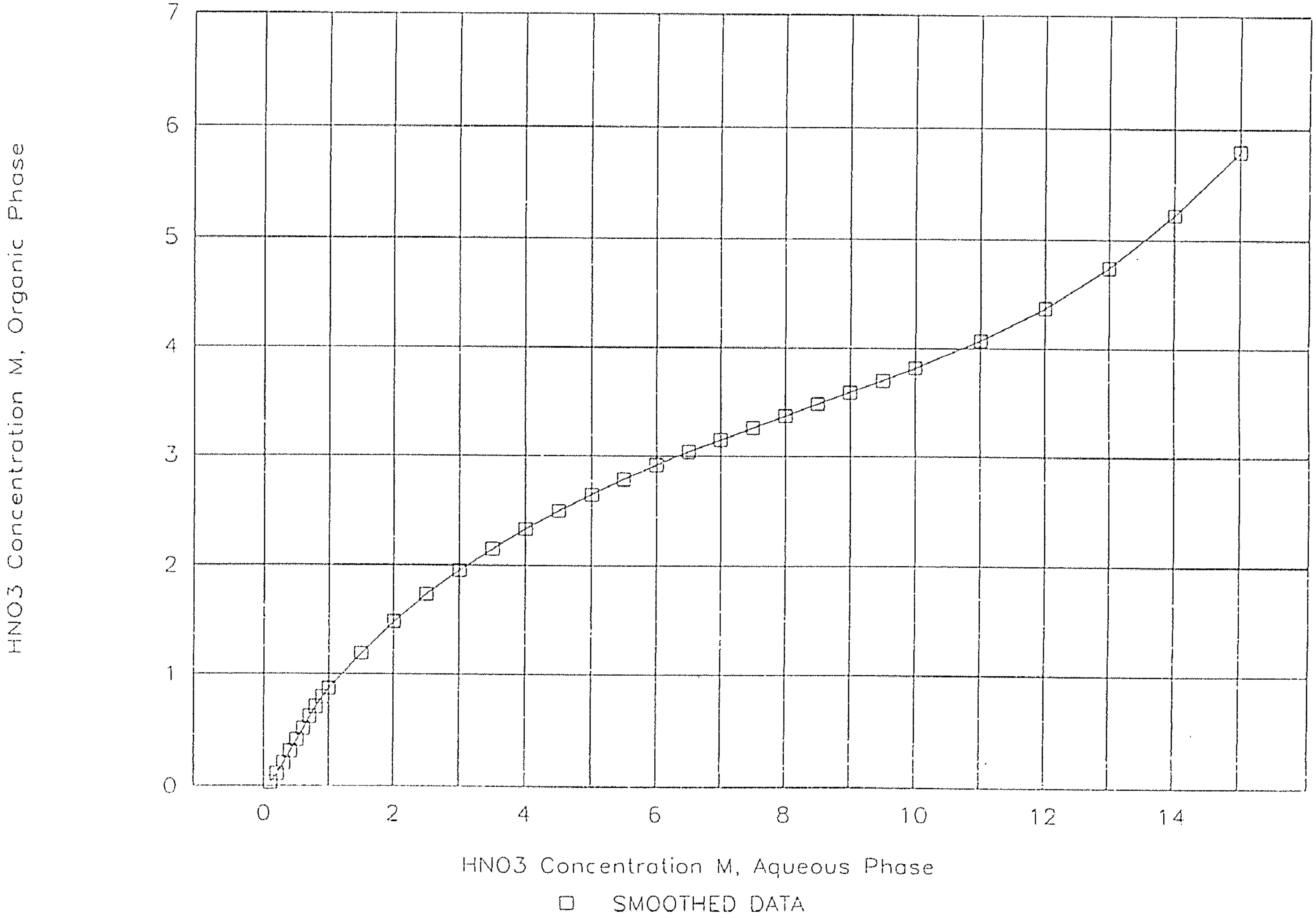

Figure 2.4 The Solubility of Nitric Acid in the TBP Phase.

is that $HNO_3 \cdot H_2O \cdot TBP$ is the chief product, through the conversion of $HNO_3 \cdot TBP$ to $HNO_3 \cdot H_2O \cdot TBP$, though other hydrates may be involved and may even be more important than the mono-hydrate.

Published data can be found in Schoenheer (3), Davis (19), Healy and Brown (22), Kinney and Smutz (23), Peppard and Ferraro (24), Shuler (25), and Davis et al. (26). Davis and his colleagues (26) smoothed all data from various sources, though the consistency of the analytical data for water is quite poor. Figure 2.5 demonstrates the solubility of water in the TBP phase as a function of nitric acid concentration in the aqueous phase.

A correlated equation was made based on the smoothed data presented by Davis and co-workers (26), so the solubility of water in the TBP phase can be built into our Liquid-liquid equilibrium model.

2.7 The Variation Of TBP Concentration In Organic Phase

As discussed in sections 2.5 and 2.6, nitrate and water molecules transfer to the organic phase through very complex chemical reactions in the HNO_3-H_2O-TBP system. The quantity of nitrate and water molecules in the organic phase depends on the nitric acid concentration in the aqueous phase. After the equilibrium is reached, the density of organic phase change slightly. Davis and co-workers (26) summarized and smoothed TBP concentrations in the organic phase from various sources. Figure 2.6 was prepared based on the

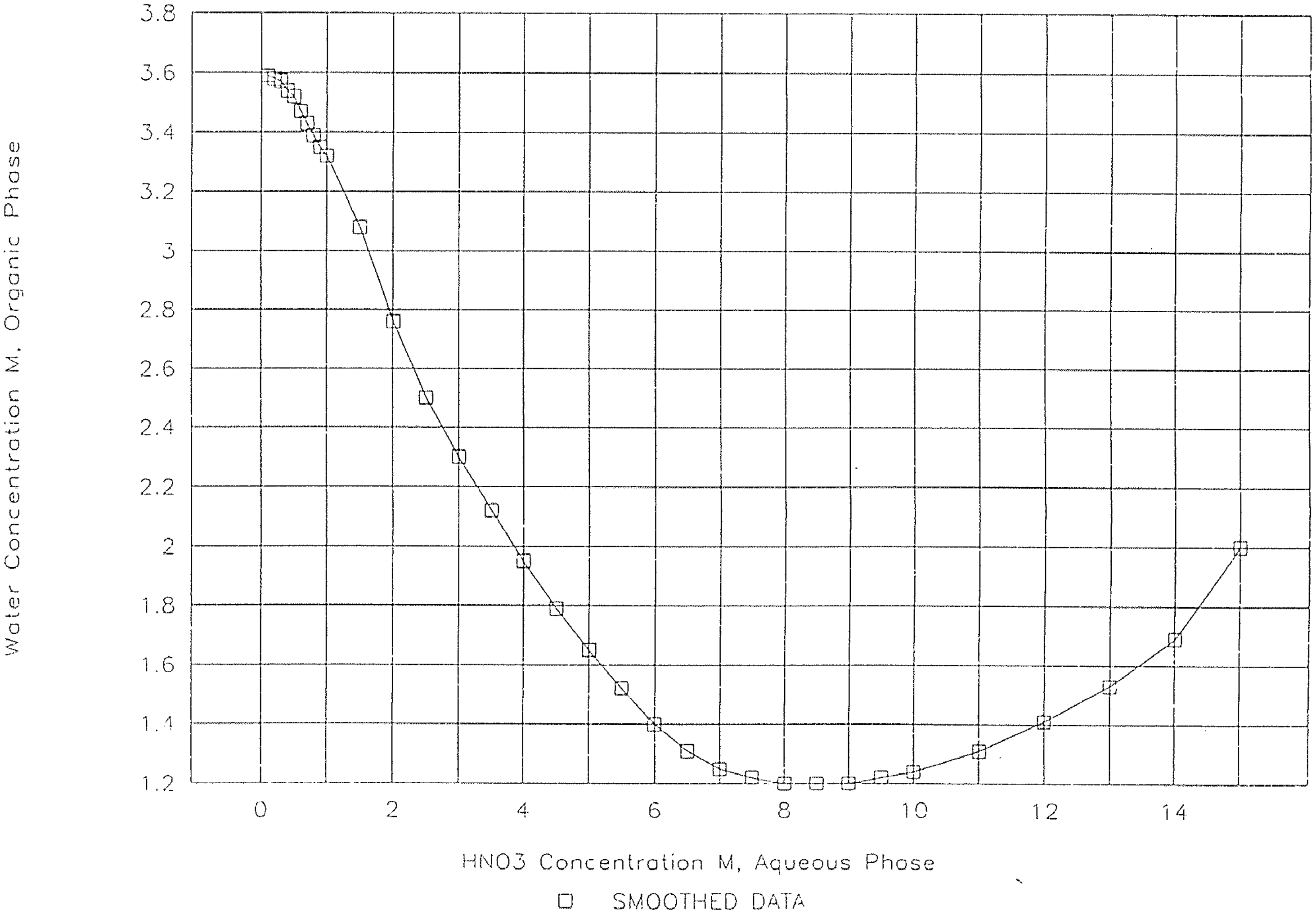

Figure 2.5 The Solubility of Water in the TBP Phase.

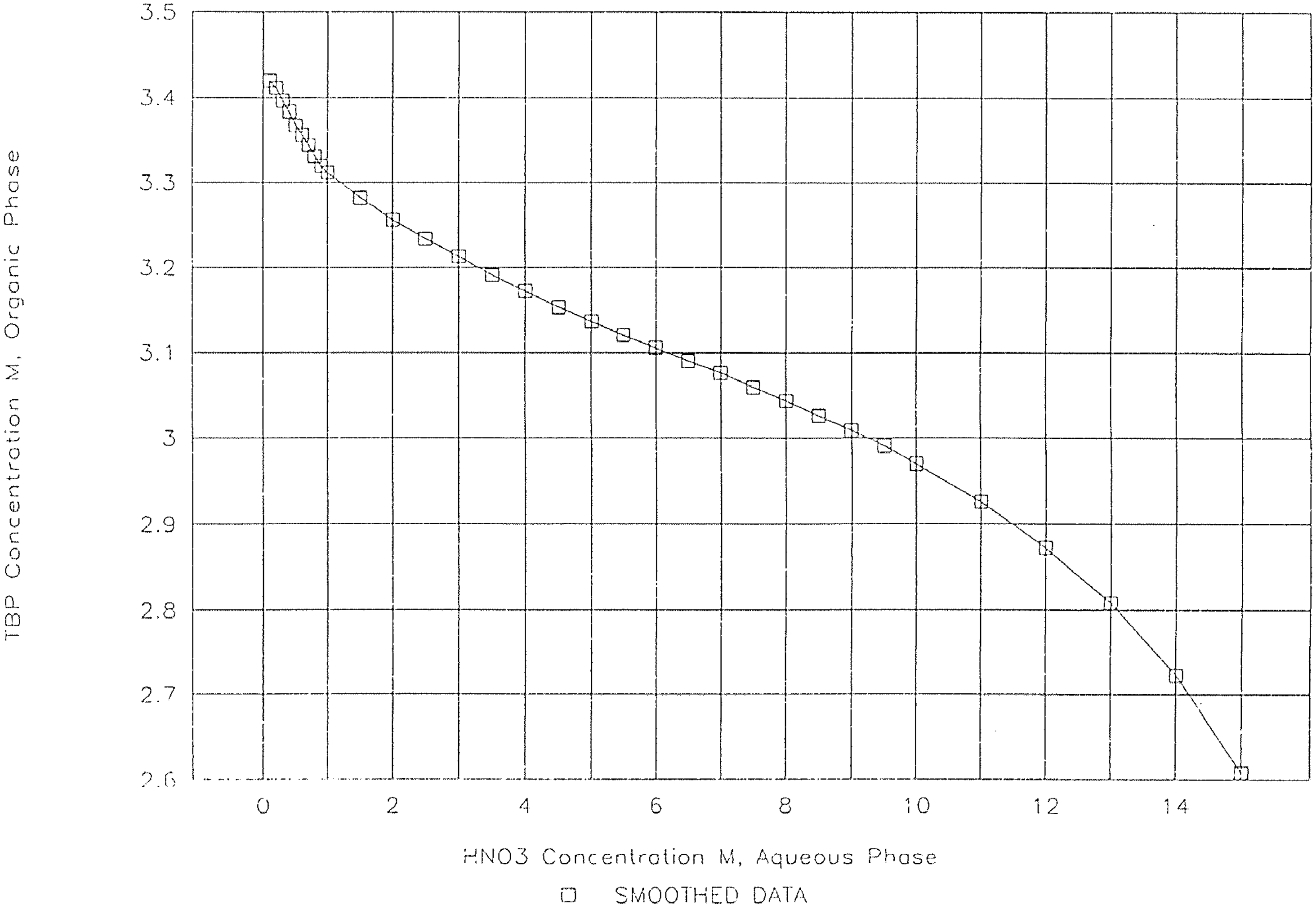

Figure 2.6 The Variation of TBP Concentration in the Organic Phase.

smoothed data presented by Davis et al. (26), which describes the variation of the TBP concentrations in the organic phase. A polynomial equation was also fitted to Davis's data and built into our equilibrium model.

2.8 The Solubility Of TBP In Aqueous Nitric Acid Solution

Baldwin and co-workers (27) and Burger and Forsman (28) reported the solubility of TBP in aqueous nitric acid to be $< 5.86 \times 10^{-3}$ mol/l over the range 0-15.6 M nitric acid. Alcock et al. (16) stated that TBP is generally less soluble in aqueous nitric acid than in pure water. Therefore, the TBP effect on most of the properties of the aqueous phase must be negligible.

2.9 The Degree Of Dissociation Of Nitric Acid

It is generally considered that nitric acid is only partially ionized and that in water the dissociation is:

$$HNO_3 = H^+ + NO_3^{-1} \qquad (2.7)$$

The equilibrium constant is:

$$K_a = \frac{[H^+] * [NO_3^{-1}]}{[HNO_3]} \qquad (2.8)$$

The literature contains a number of attempts to measure the dissociation constant of nitric acid (29), (30), (31), (32), (33), (34). Davis and Bruin (35) obtained some new experimental data on liquid-vapor equilibrium in the system HNO_3-H_2O by the transpiration technique. They combined new data and literature values on partial pressure of nitric acid with an activity coefficient derived from freezing point measurements to calculate the stoichiometric activity coefficients of nitric acid from the concentration range 0 to 100 per cent acid. This first requires evaluation of the ratio of the stoichiometric activity coefficients of nitric acid in the pure and infinitely dilute solutions. Water activities were then readily obtained by means of the Gibbs-Duhem equation. Finally, they combined the stoichiometric activity coefficients with published data for the degree of dissociation to obtain a consistent set of values of the degree of dissociation and of the mean ionic and molecular activity coefficients.

Figure 2.7 shows the nitric acid degree of dissociation of nitric acid in the aqueous phase. Figure 2.8 shows the ionization of aqueous nitric acid at 25^{o}C. Because of the incomplete dissociation of nitric acid in the aqueous phase, NO_3^{-1} indeed rises to a maximum of 5.1 M at an acidity of 9.0 M at 25^{o}C and then falls.

The consistent data developed by Davis and Bruin (35) were fitted into a polynomial equation, so the nitric acid dissociation constant can be build into our equilibrium model.

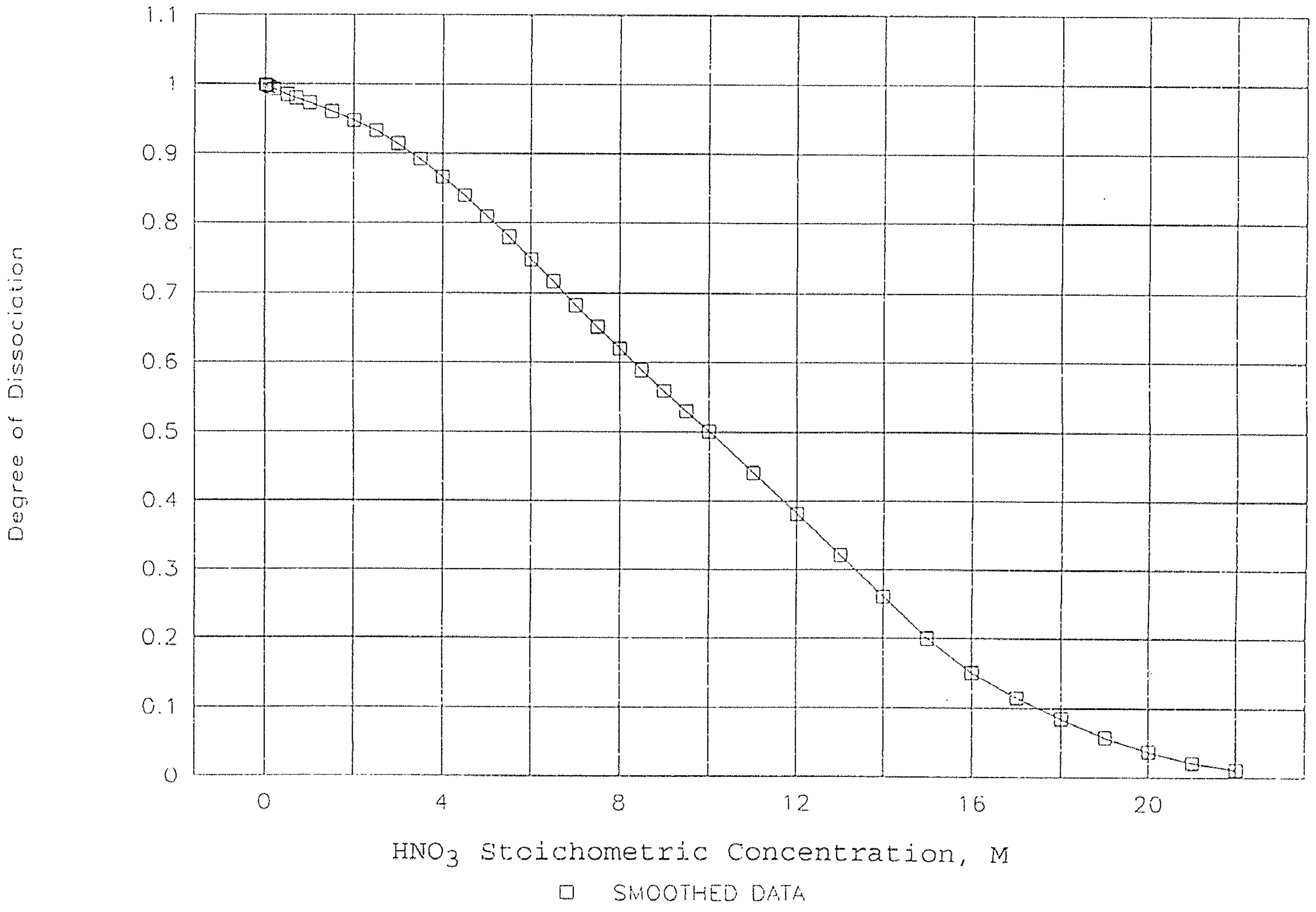

Figure 2.7 The Nitric Acid Degree of Dissociation.

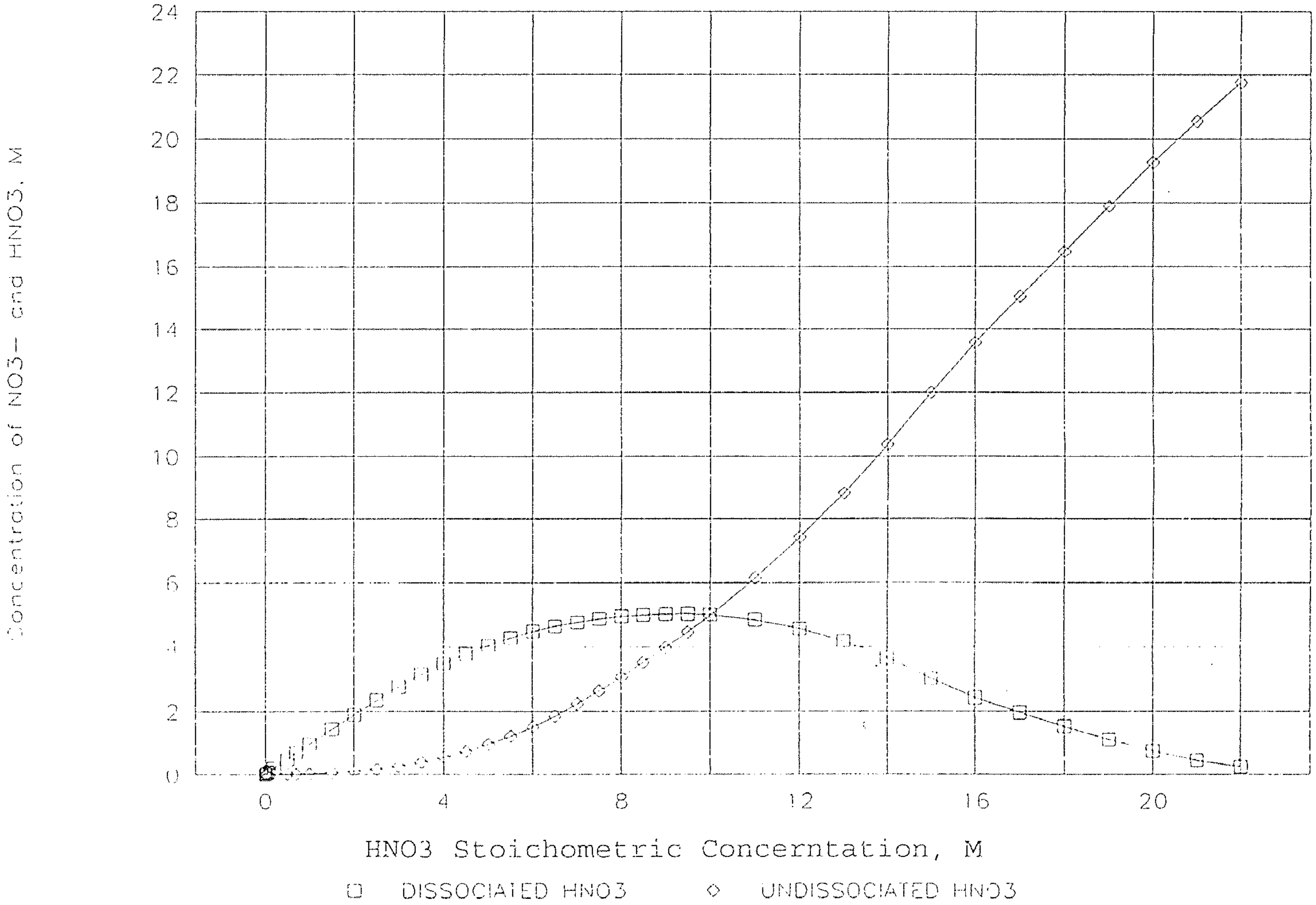

Figure 2.8 The Ionization of Aqueous Nitric Acid at 25°C.

2.10 The Stability Constants Of Rare Earth Complexes In Aqueous Solution

The thermodynamic stability of a complex can be indicated by an equilibrium constant relating its concentration to the concentration of other species when the system has reached equilibrium. If a solution contains aquated metal ions M and unidentate ligands L, and only soluble mononuclear complexes are formed, then the system at equilibrium may be described by the following equations and equilibrium constants:

$$M + L = ML \qquad K1 = \frac{[ML]}{[M] * [L]} \tag{2.9}$$

$$M + 2L = ML_2 \qquad K_2 = \frac{[ML_2]}{[M] * [L]^2} \tag{2.10}$$

$$M + 3L = ML_3 \qquad K_3 = \frac{[ML_3]}{[M] * [L]^3} \tag{2.11}$$

$$\vdots \qquad\qquad\qquad\qquad \vdots$$

$$M + NL = ML_N \qquad K_N = \frac{[ML_N]}{[M] * [L]^N} \tag{2.12}$$

There will be N such equilibria, where N represents the maximum coordination number of the metal ion M for ligand L, and N may vary from one ligand to another. The K_i's are called the overall stability constants.

Owing to its +3 charge the rare earth ion forms stable complexes with many anions such as chloride, nitrate, and sulfate. In general, the degree to which these complexes form is dependent only on the total ionic strength of the solution. The complexing reactions for rare earth nitrate are:

$$M^{+3} \quad + \quad NO_3^{-1} \quad \overset{K_1}{====} \quad MNO_3^{+2} \qquad (2.13)$$

$$M^{+3} \quad + \quad 2NO_3^{-1} \quad \overset{K_2}{====} \quad M(NO_3)_2^{+1} \qquad (2.14)$$

$$M^{+3} \quad + \quad 3NO_3^{-1} \quad \overset{K_3}{====} \quad M(NO_3)_3 \qquad (2.15)$$

Choppin and Strazik (36) have determined that rare earth nitrate complexes are out-sphere in nature, a monolayer of water molecules separate the nitrate and rare earth. This layer of water acts as a dielectric and reduces the strength of the ionic bond that forms the complex. The neutral species $M(NO_3)_3$ is present only when the rare earth nitrate concentrations approaching the solubility limit. Since all solutions involved in this research were below the solubility limit, therefore, the neutral species $M(NO_3)_3$ is considered non-existent.

The stability constants for rare earth complexes in the aqueous phase are:

$$K_1 = \frac{[MNO_3^{+2}]_A}{[M^{+3}]_A * [NO_3^{-1}]_A} \tag{2.16}$$

$$K_2 = \frac{[M(NO_3)_2^{+1}]_A}{[M^{+3}]_A * [NO_3^{-1}]_A^2} \tag{2.17}$$

$$K_3 = 0 \tag{2.18}$$

Efforts have been made by Choppin and Strazik (36), Peppard et al. (37), Panova et al. (38), Fomin et al (39), Bansal et al (40) and Batyaev et al. (41) to determine the rare earth nitrate stability constants. These experimentally obtained stability constants will be used in Section 4.2 as initial value of model parameters.

2.11 The Experimental Data Of The Extraction Of Rare Earth Nitrate By 100% TBP

Many publications gave data in the distribution of rare earths in the tri-n-butyl phosphate (TBP) - nitric acid system (42), (43), (44), (45), (46), (47), (48), (49), (50), (51). The experimental results have shown the effective way to separate rare earths in the HNO_3-H_2O-TBP two-phase system is with 12-18 M HNO_3. With TBP, the extraction of rare earth nitrate into the organic phase increases in the order of increased atomic number, and with higher yttrium extractability (42). The most comprehensive set of distribution coefficients for extraction from HNO_3 are two publications from the UK Harwell Laboratory (12), (52). Radioactive trace rare earth oxides were prepared from a solution of fission products in nitric acid by extraction first into 19% TBP in kerosene from 8 M HNO_3. After a series of stripping and extracting purification procedures, the radioactive tracer (< 1 g/l, or < 0.01 M) was in the HNO_3 solution and ready for experiments. TBP is generally purified by boiling 100 ml crude or impure TBP with 500 ml of 0.4% caustic soda solution at atmospheric pressure until 200 ml of distillate has collected. Volatile impurities come over with the steam. The TBP remaining in the distillation flask is washed repeatedly with water and dried by warming under vacuum condition. The distribution coefficients were determined by stirring 5 ml of each phase together in a centrifuge tube for up to 60 minutes, centrifuging, and separating the phases for analysis. The distribution coefficients were measured with aqueous solution acidities 0.3-18 M, and with 100% TBP. All measurements were made at $25^{o}C$.

Distribution coefficients for a total of 16 rare earths, namely, lutetium, yttrium, ytterbium, thulium, erbium, holmium, dysprosium, terbium, gadolinium, europium, samarium, promethium, neodymium, praseodymium, cerium, and lanthanum, have been determined and tabulated with sufficiently small intervals, that almost any desired data can be interpolated or extrapolated. Graphics are also presented. Plotting of the data demonstrates these main characteristics of behavior of the elements: the initial steep rise in the curves at low acidities; most form a maximum-minimum curve in the HNO_3 4-8 M region; then a further steep rise at a faster path at higher acidities (HNO_3 > 10 M). Figure 2.9 shows a graphical presentation of all of the 16 rare earth elements distribution coefficient curves (63).

Scargill and co-workers (51) hypothesized that the characteristics of distribution coefficient curves are dominated by the following factors: salting-out from the aqueous phase by the nitrate ion at lower acidities; formation of nitrate complexes and nitric acid competition for the available TBP at moderate HNO_3 concentrations; and activity coefficient effects at high acidities.

Because Harwell Laboratory experimental results were obtained for micro-amounts of rare earth elements, Mikhlin and Korpusov (53) measured the distribution of macro-amounts of gadolinium, terbium, dysprosium, and yttrium between TBP and 8, 10, 12 and 14 N HNO_3. For the same acidity, the distribution coefficient depends on the equilibrium rare earth concentration in the aqueous phase. With an increase in the rare earth equilibrium concentration there is a drop in the distribution coefficient owing to the decrease in the free solvent concentration. They also observed the order of increase in extractability with increase in atomic number of the element is the same for macro-amounts of rare earths as for micro-quantities (42). Their results indicate the degree of separation of these elements and the position of yttrium in the rare earths series depends on both the nitric acid concentration and the rare earth concentration.

The Harwell Laboratory experimental data were used to determine the parameters of our rare earths liquid-liquid equilibrium model.

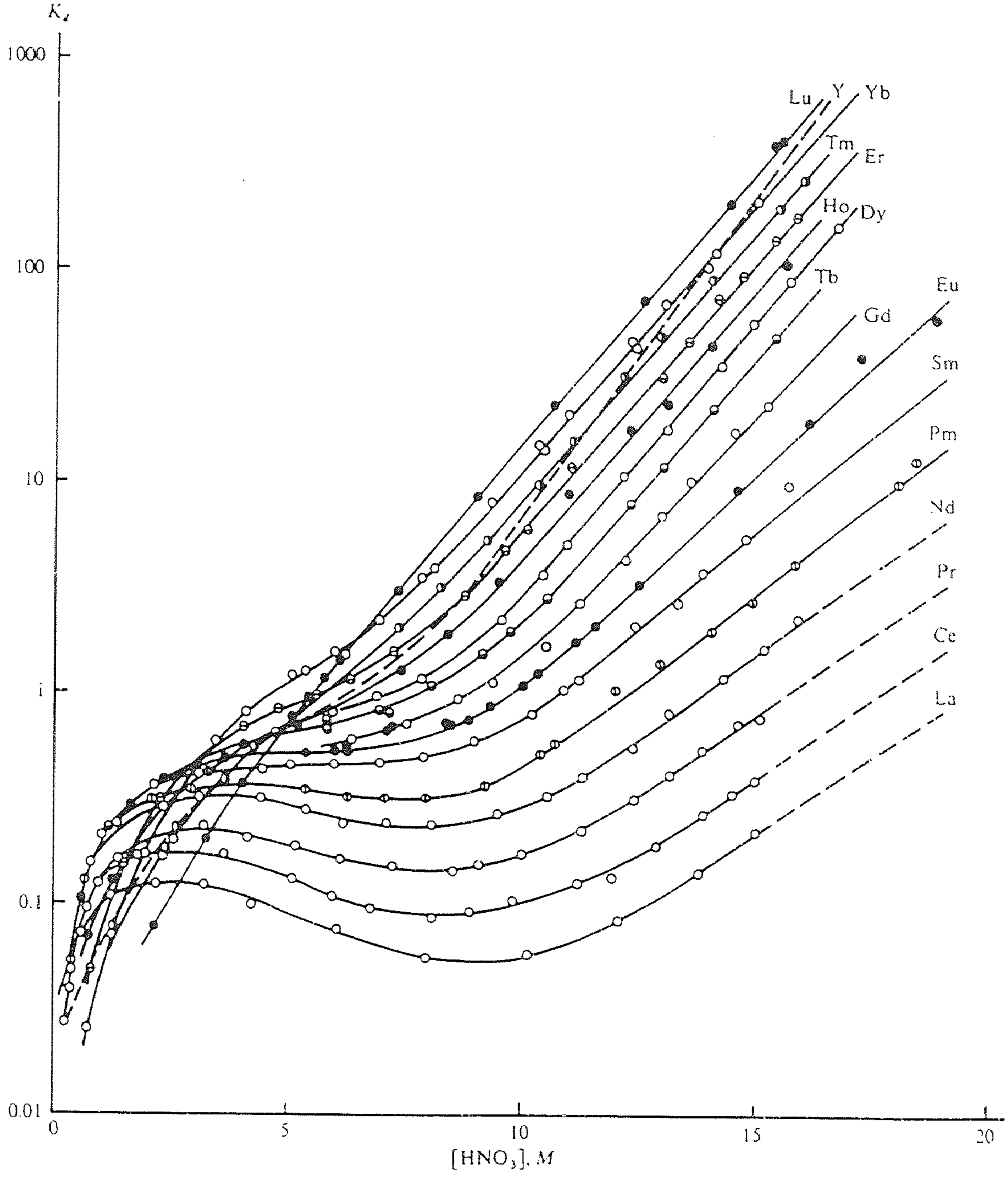

Figure 2.9 Distribution of Rare Earth Elements between 100% TBP and Aqueous Solution of HNO_3 as a Function of the Initial HNO_3 Concentration. Initial Concentration of Rare Earth Elements < 1 g/l; 25°C; Contact Time up to 60 Minutes.

CHAPTER 3

DEVELOPMENT OF LIQUID-LIQUID EQUILIBRIUM MODEL

3.1 Basic Assumptions

Having the theoretical background discussed in Chapter 2, let us assume that a nitric acid solution with an initial concentration $(HNO_3)_{AI}$ with a trace of rare earth oxides with an initial concentration $(RRE)_{AI}$ dissolved in it, is equilibrated with an equal volume of TBP solvent with an initial concentration $(TBP)_{OI}$ in a container at 25°C. After settling, two immiscible phases co-exist: aqueous phase and organic phase. The subscript I refers to **initial**.

Let us further assume that there is no volume change in either the aqueous phase or the organic phase after mixing and settling. Thus, the chemical species which can be found in the aqueous phase and the organic phase after settling are:

In the aqueous phase:

$$HNO_3,\ H_2O,\ H^+,\ NO_3{}^{-1},\ M^{+3},\ MNO_3{}^{+2},\ M(NO_3)_2{}^{+1}$$

In the organic phase:

$$TBP,\ HNO_3\cdot TBP \text{ complexes},\ H_2O,\ M(NO_3)_3\cdot(TBP)_3$$

Where M^{+3} refers to rare earth ion with three charges. Parameters involved in chemical reactions are:

K_d, SF, K_e, K_a, K_1, K_2

With the theoretical knowledge of rare earths compound (RRE) in the HNO_3-H_2O-TBP two-phase system, coupled with the basic assumptions made in this section, the liquid-liquid extraction equilibrium model is now ready for development.

3.2 The Equilibrium Constant For The Complex Of Rare Earth Nitrate And TBP

Section 2.2 discussed the rare earth nitrate and the TBP complex formation in the HNO_3-H_2O-TBP system. Equation (2.3) demonstrates the complex formation, and equation (2.4) expresses the equilibrium constant. Since the activity of a specific chemical compound is the product of the concentration and the activity coefficient of that compound at the same temperature, then, equation (2.4) can be expressed as:

$$K_e = \frac{(M(NO_3)_3(TBP)_3)_O}{(M^{+3})_A * (NO_3^{-1})_A^3 * (TBP)_O^3} * \frac{[[M(NO_3)_3(TBP)_3]]_O}{[[M^{+3}]]_A * [[NO_3^{-1}]]_A^3 * [[TBP]]_O^3} \tag{3.1}$$

Let us define:

$$K_e' = \frac{(M(NO_3)_3(TBP)_3)_O}{(M^{+3})_A * (NO_3^{-1})_A^3 * (TBP)_O^3} \tag{3.2}$$

And again define:

$$K_{re} = \frac{[[M(NO_3)_3(TBP)_3]]_O}{[[M^{+3}]]_A * [[NO_3^{-1}]]_A^3 * [[TBP]]_O^3} \tag{3.3}$$

Thus

$$K_e = K_e' * K_{re} \tag{3.4}$$

The double brackets [[ ]] here refer to **activity coefficients**. All three equilibrium constants are functions of physical properties in the aqueous phase and the organic phase. Even though they are all equilibrium constants, they each have their own distinct physical definitions. K_e is the equilibrium constant of the complex formation for species M^{+3}, NO_3^{-1} and TBP, if the reaction is expressed in terms of chemical activities. K_e' is the equilibrium constant, if the reaction is expressed in terms of concentrations. K_{re} is the equilibrium constant, if the reaction is expressed in terms of activity coefficients. By definitions of chemical equilibrium and chemical activity, only the activity equilibrium constant is truly a constant.

3.3 The Stability Constants For The Complex Of Rare Earth Nitrate In Aqueous Phases

The stability constants for rare earth nitrate complex in the aqueous phase were discussed in Section 2.10. Because of their similarity in nature, the stability constants will be treated in the same manner in Section 3.2 for the rare earth nitrate and TBP complex equilibrium constants.

Express equation (2.16) and (2.17) by concentrations and activity coefficients:

$$K_1 = \frac{(MNO_3{}^{+2})_A}{(M^{+3})_A * (NO_3{}^{-1})_A} * \frac{[[MNO_3{}^{+2}]]^A}{[[M^{+3}]]_A * [[NO_3{}^{-1}]]_A} \tag{3.5}$$

$$K_2 = \frac{(M(NO_3)_2{}^{+1})_A}{(M^{+3})_A * (NO_3{}^{-1})_A{}^2} * \frac{[[M(NO_3)_2{}^{+1}]]_A}{[[M^{+3}]]_A * [[NO_3{}^{-1}]]_A{}^2} \tag{3.6}$$

Define:

$$K_1' = \frac{(MNO_3{}^{+2})_A}{(M^{+3})_A * (NO_3{}^{-1})_A} \tag{3.7}$$

$$K_2' = \frac{(M(NO_3)_2{}^{+1})_A}{(M^{+3})_A * (NO_3{}^{-1})_A{}^2} \tag{3.8}$$

$$K_{r1} = \frac{[[M^{+3}]]_A * [[NO_3{}^{-1}]]_A}{[[MNO_3{}^{+2}]]_A} \tag{3.9}$$

$$K_{r2} = \frac{[[M^{+3}]]_A * [[NO_3{}^{-1}]]_A{}^2}{[[M(NO_3)_2{}^{+1}]]_A} \qquad (3.10)$$

Combining equations (3.5), (3.6), (3.7), (3.8), (3.9) and (3.10), we have:

$$K_1' = K_1 * K_{r1} \qquad (3.11)$$

$$K_2' = K_2 * K_{r2} \qquad (3.12)$$

Equilibrium constants K_{r1} in equation (3.9) and K_{r2} in equation (3.10) are the functions of the activity coefficients in the aqueous phase only. As we mentioned in Section 3.2, only the activity equilibrium constants K_1 and K_2 are true constants among all six equilibrium constants in this section.

Because traces of rare earth exists in the aqueous solution initially, and most of rare earth nitrate forms complex $M(NO_3)_3(TBP)_3$ with TBP and transfers to the organic phase, then the rare earth ions that remain in the aqueous phase and form complexes $MNO_3{}^{+2}$ and $M(NO_3)_2{}^{+1}$ are in micro-quantity. Based on Henry's law activity coefficient (54), in infinite dilution, the solute activity coefficient approaches unity as the mole fraction goes to zero. In order words, activity coefficients $[[M^{+3}]]_A$, $[[MNO_3{}^{+2}]]_A$ and $[[M(NO_3)_2{}^{+1}]]_A$ all equal or approach to one. Thus,

$$K_1' = K_1 * [[NO_3^{-1}]]_A \tag{3.13}$$

$$K_2' = K_2 * [[NO_3^{-1}]]_A^2 \tag{3.14}$$

Assume that the nitrate activity coefficient $[[NO_3^{-1}]]_A$ varies only slightly at a specific acidity in the aqueous phase. Therefore, the equilibrium constants can be simply expressed only by the chemical specie concentrations.

3.4 The Correlation For Nitric Acid In The Organic Phase

We have discussed the distribution of nitric acid in aqueous and TBP organic phase in Section 2.5. Because numerous forms of $HNO_3 \cdot TBP$ complex exist in the organic phase, and the number of complex formulas are still not yet determined, it is not possible to calculate the equilibrium constant for each complex formation. Therefore, for mathematical modelling purposes, the concept of nitric acid solubility in the organic phase was introduced. The smooth data prepared by Davis and his colleagues (26) for the nitric acid solubility in the TBP organic phase was fitted to the following correlation formula:

$$((HNO_3)_n \cdot TBP)_O = -0.07272 - 1.062423*(HNO_3)_{AT} -$$

$$0.173784*((HNO_3)_{AT})**2 + 0.0186665*((HNO_3)_{AT})**3 -$$

$$0.001062*((HNO_3)_{AT})**4 + 0.0000261*((HNO_3)_{AT})**5 \tag{3.15}$$

The formula $((HNO_3)_n{\cdot}TBP)_O$ in equation (3.15) is defined as solubility of nitric acid in the organic phase, in mole per liter of solution. The symbol $(HNO_3)_n{\cdot}TBP$ is the hypothetical formula, which includes all forms of $HNO_3{\cdot}TBP$ complexes in the organic phase for a specific nitric acid concentration in the aqueous phase. The subscript **n** here refers to the **number of moles** of HNO_3 in the complex associated with **each** molecule of TBP.

3.5 Material Balance For Nitrate $NO3^{-1}$

The previous section defined the formula of $((HNO_3)_n{\cdot}TBP)_O$. Since the nitrate NO_3^{-1} exists in both phases, then the material balance for nitrate NO_3^{-1} is:

$$(HNO_3)_{AI} = (HNO_3)_{AT} + ((HNO_3)_n{\cdot}TBP)_O +$$

$$3(M(NO_3)_3(TBP)_3)_O + (MNO_3^{+2})_A + 2(M(NO_3)_2^{+1})_A \qquad (3.16)$$

The subscript **T** here means the **total free** nitric acid in aqueous phase after equilibrium is reached. In other words, $(HNO_3)_{AT}$ is the **total unreacted** nitric acid in the aqueous phase. The nitric acid will dissociate, as we discussed in Section 2.9, therefore, $(HNO_3)_{AT}$ should be considered to be the **sum** of **dissociated** and **undissociated** nitric acid in the aqueous phase after the chemical reaction equilibrium has been reached. The compounds $M(NO_3)_3(TBP)_3$

and $M(NO_3)_2^{+1}$ in equation (3.16) must be multiplied by the number of nitrates complex with rare earth ion.

3.6 Material Balance For Tri-n-Butyl Phosphate (TBP)

As discussed in Section 2.8, the solubility of TBP in the aqueous phase is small and its effect on the properties of the aqueous phase is negligible. Thus, TBP is considered to exist in the organic phase only. The material balance for TBP in entire system is :

$$(TBP)_{AI} = (TBP)_O + ((HNO_3)_n \cdot TBP)_O/NOH +$$

$$3(M(NO_3)_3(TBP)_3)_O \qquad (3.17)$$

where the denominator **NOH** is defined as the **number of nitric acid moles** in conjunction with each TBP molecule in the complex. Thus, the subscript n and denominator NOH share the same definition. Because concentration of $((HNO_3)_n \cdot TBP)_O$ is specified in terms of molarity, which is expressed as the number of moles of HNO_3 per liter of solution, therefore, the number of moles of TBP in the complex $((HNO_3)_n \cdot TBP)_O$ is obtained by dividing $((HNO_3)_n \cdot TBP)_O$ concentration with NOH. NOH is not a constant, but varies when the acidity changes in the aqueous phase.

Three moles of TBP are attached in each mole of $M(NO_3)_3(TBP)_3$, thus the concentration of TBP is three times of $M(NO_3)_3(TBP)_3$ concentration.

3.7 Material Balance For Rare Earth Nitrate

The rare earth nitrate transfers from the aqueous phase to the organic phase by forming $M(NO_3)_3(TBP)_3$ complexes with TBP in the organic phase. Therefore, the rare earth species exist both in the aqueous and the organic phases. The following equation (3.18) describe the material balance for rare earth species (RRE):

$$(RRE)_{AI} = (M^{+3})_A + (M(NO_3)_3(TBP)_3)_O + (MNO_3^{+2})_A + (M(NO_3)_2^{+1})_A \qquad (3.18)$$

Combining equations (3.2), (3.7), (3.8) and (3.18) and eliminating $(M(NO_3)_3(TBP)_3)_O$, $(MNO_3^{+2})_A$ and $(M(NO_3)_2^{+1})_A$ in equation (3.18):

$$(RRE)_{AI} = (M^{+3})_A + K_e'*(M^{+3})_A*(NO_3^{-1})_A^3*(TBP)_O^3 + K_1'*(M^{+3})_A*(NO_3^{-1})_A + K_2'*(MNO_3^{+2})_A*(NO_3^{-1})_A \qquad (3.19)$$

After rearranging:

$$(RRE)_{AI} = (M^{+3})_A*(1 + K_e'*(NO_3^{-1})_A^3*(TBP)_O^3 + K_1'*(NO_3^{-1})_A + K_2'*(NO_3^{-1})_A^2) \qquad (3.20)$$

Consequently, the concentration of rare earth ion M^{+3}

in the aqueous phase can be expressed by initial rare earth concentration, nitrate concentration and chemical equilibrium constants.

3.8 The Correlation For Nitrate $NO3^{-1}$ Concentration

As discussed in Section 2.9, nitric acid is only partially ionized:

$$HNO_3 = H^+ + NO_3^{-1} \qquad (2.7)$$

The Davis and Burin's consistent data (35) for the nitric acid degree of dissociation (DOD) were fitted into a polynomial equation:

$$DOD = 1.0006204 - 0.020407*(HNO_3)_{AT} - 0.004496*((HNO_3)_{AT})**2 + 0.0001546*((HNO_3)_{AT})**3 \qquad (3.21)$$

The degree of dissociation (DOD) is the ratio of nitrate concentration $(NO_3^{-1})_A$ to total unreacted nitric acid $(HNO_3)_{AT}$ in the aqueous phase, thus the concentration of $(NO_3^{-1})_A$ is readily obtained:

$$(NO_3^{-1})_A = DOD*(HNO_3)_{AT} \qquad (3.22)$$

Eliminating DOD in equation (3.22) by combining equations (3.21) and (3.22):

$$(NO_3^{-1})_A = 1.0006204*(HNO_3)_{AT} - 0.020407*((HNO_3)_{AT})**2$$

$$- 0.004496*((HNO_3)_{AT})**3 + 0.0001546*((HNO_3)_{AT})**4 \quad (3.23)$$

From equation (3.23), nitrate concentration can be easily calculated if $(HNO_3)_{AT}$ is given.

3.9 Material Balance For Hydrogen Atoms H

The rare earth ion M^{+3} has three charges, since the rare earth ions are extracted by a cation-exchange solvent, one mole of the rare earth extraction is accompanied by a discharge of three moles of hydrogen ion into the aqueous phase. Analogous to equation (2.3), we have:

$$(M^{+3})_A + (3/2)*(O^{-2})_A + 3(H^+)_A + 3(NO_3^{-1})_A + 3(TBP)_O =$$

$$(M(NO_3)_3(TBP)_3)_O + 3(H_2O)_A \quad (3.24)$$

Trace of rare earth $(RRE)_{AI}$ initially exists in this HNO_3-H_2O-TBP two-phase system, and micro-quantities of $(M^{+3})_A$, $(M(NO_3)_2^{+1})_A$ and $(MNO_3^{+2})_A$ exist after equilibrium has been reached. For mathematical modeling purposes, it is assumed that almost all initial rare earths in the aqueous solution $(RRE)_{AI}$ have formed the $(M(NO_3)_3(TBP)_3)_O$ complex and have been extracted. Therefore, the initial rare earths $(RRE)_{AI}$ and $(M(NO_3)_3(TBP)_3)_O$ complexes have identical molarity, if volume does not change in both phases after equilibrium has been established. It is convenient to set the hydrogen consumption during extraction process equal to one third of the $(RRE)_{AI}$.

$$(H^{+})_{consumed} = (1/3)*(RRE)_{AI} \tag{3.25}$$

Or replace $(RRE)_{AI}$ by equation (3.20)

$$(H^{+})_{consumed} = (1/3)*(M^{+3})_{A}*(1 + K_{e}'*(NO_{3}^{-1})_{A}^{3}*(TBP)_{O}^{3} + K_{1}'*(NO_{3}^{-1})_{A} + K_{2}'*(NO_{3}^{-1})_{A}^{2}) \tag{3.26}$$

The material balance for hydrogen atoms H around HNO_3-H_2O-TBP two-phase system:

$$(HNO_{3})_{AI} = (1\text{-}DOD)*(HNO_{3})_{AT} + (H^{+})_{A} + (H^{+})_{consumed} + ((HNO_{3})_{n}\cdot TBP)_{O} \tag{3.27}$$

Combining equation (3.25) and equation (3.27):

$$(HNO_{3})_{AI} = (1\text{-}DOD)*(HNO_{3})_{AT} + (H^{+})_{A} + (1/3)*(RRE)_{AI} + ((HNO_{3})_{n}\cdot TBP)_{O} \tag{3.28}$$

Or combine equation (3.26) and equation (3.27):

$$(HNO_3)_{AI} = (1\text{-}DOD)*(HNO_3)_{AT} + (H^+)_A + ((HNO_3)_n \cdot TBP)_O +$$

$$(1/3)*(M^{+3})_A*(1 + K_e'*(NO_3{}^{-1})_A{}^3*(TBP)_O{}^3 +$$

$$K_1'*(NO_3{}^{-1})_A + K_2'*(NO_3{}^{-1})_A{}^2) \qquad (3.29)$$

As we discussed in Section 3.5, $(HNO_3)_{AT}$ is the sum of dissociated and undissociated nitric acid in the aqueous phase. The term $(1\text{-}DOD)*(HNO_3)_{AT}$ in equation (3.29) represents the undissociated nitric acid after equilibrium has been reached.

3.10 The TBP Concentration In The Organic Phase

The variation of TBP concentration in the organic TBP solution was discussed in Section 2.7. Davis's smoothed data (26) was regressed to yield:

$$(TBP)_O = 3.428093 - 0.13173*(HNO_3)_{AT} +$$

$$0.028538*((HNO_3)_{AT})**2 - 0.003824 *((HNO_3)_{AT})**3 +$$

$$0.0002462*((HNO_3)_{AT})**4 - 0.000006359*((HNO_3)_{AT})**5$$

$$(3.30)$$

3.11 The Distribution Coefficients For Nitric Acid In The HNO_3-H_2O-TBP System

All discussions of the distribution coefficients so far have been focused on the distribution of rare earths in the HNO_3-H_2O-TBP two-phase system. We also mentioned that nitric acid will form various complexes with TBP in the organic phase. Davis and co-workers (26) reported the distribution of nitric acid between the aqueous and the 100% TBP phase, after analyzing experimental data from different sources. Concentrations of nitric acid in both phases were given, so the distribution coefficients of nitric acid in the HNO_3-H_2O-TBP system can be easily calculated and correlated into polynomial form:

$$(K_d)_{nitric\ acid} = -25.4334 + 12.115960*(HNO_3)_{AT} - 10.24788*((HNO_3)_{AT})**2 + 26.14166*((HNO_3)_{AT})**3 - 5.342299*((HNO_3)_{AT})**4 \quad (3.31)$$

Equation (3.31) will be used in the multicomponent multistage counter-current liquid-liquid extraction computer program.

3.12 The Distribution Coefficients For Water In The HNO_3-H_2O-TBP System

Davis et al. (26) also reported the distribution of water between the aqueous and the 100% TBP phase. Concentrations of water in the organic phases were given, densities of aqueous solution along with different equilibrium nitric acid concentrations were also given, by the help of liquid densities, the concentrations of water in the aqueous solution were calculated, and the distribution coefficients of water in the HNO_3-H_2O-TBP system can be readily obtained and correlated into the following formula:

$$(K_d)_{water} = 0.5196597 - 4.46808*(HNO_3)_{AT} + 19.72675*((HNO_3)_{AT})**2 - 32.13729*((HNO_3)_{AT})**3 + 19.22704*((HNO_3)_{AT})**4 \qquad (3.32)$$

Equation (3.32) will also be used in the multicomponent multistage counter-current liquid-liquid extraction computer program.

3.13 Construction of Distribution Coefficients For Rare Earths

The distribution coefficient K_d of rare earths in the HNO_3-H_2O-TBP system also can be expressed by:

$$K_d = \frac{\text{Concentration of } M^{+3} \text{ in organic phase}}{\text{Concentration of } M^{+3} \text{ in aqueous phase}} \qquad (3.33)$$

From Section 3.1, the chemical species including M^{+3} the organic phase is $M(NO_3)_3(TBP)_3$, and in the aqueous phase are: M^{+3}, $MNO_3{}^{+2}$, $M(NO_3)_2{}^{+1}$, thus we have:

$$K_d = \frac{(M(NO_3)_3(TBP)_3)_O}{(M^{+3})_A + (MNO_3^{+2})_A + (M(NO_3)_2^{+1})_A} \tag{3.34}$$

Combining equations (3.2), (3.7), (3.8) and (3.34) and eliminating (M^{+3}) in numerator and denominator , we obtained:

$$K_d = \frac{K_e'*(NO_3^{-1})_A^3*(TBP)_O^3}{1 + K_1'*(NO_3^{-1})_A + K_2'*(NO_3^{-1})_A^2} \tag{3.35}$$

Eliminating K_e', $K_1'$and K_2' in equation (3.35) by substituting equations (3.4), (3.13) and (3.14) into equation (3.35):

$$K_d = \frac{(K_e/K_{re})*(NO_3^{-1})_A^3*(TBP)_O^3}{(1 + K_1*(NO_3^{-1})_A*[[NO_3^{-1}]]_A + K_2*(NO_3^{-1})_A^2*[[NO_3^{-1}]]_A^2)} \tag{3.36}$$

Expressing K_{re} in activity coefficients by combining equations (3.3) and (3.36):

$$K_d = \frac{K_e*(NO_3^{-1})_A^3*(TBP)_O^3}{(1 + K_1*(NO_3^{-1})_A*[[NO_3^{-1}]]_A + K_2*(NO_3^{-1})_A^2*[[NO_3^{-1}]]_A^2)} * \frac{[[M^{+3}]]_A*[[NO_3^{-1}]]_A^3*[[TBP]]_O^3}{[[M(NO_3)_3(TBP)_3]]_O} \tag{3.37}$$

Equation (3.37) is a very complicated form. It consists of the nitrate concentration $(NO_3^{-1})_A$, the TBP concentration $(TBP)_O$, the stability constants K_1 and K_2, the activity equilibrium constant K_e, and the activity coefficients $[[M^{+3}]]_A$, $[[NO_3^{-1}]]_A$, $[[TBP]]_O$ and $[[M(NO_3)_3(TBP)_3]]_O$ in both the aqueous phase and the organic phase. Without simplification, equation (3.37) has very little practical value.

Suppose there is a function, which is analogous to the Redlich-Kister expansion (55), that can accurately express the characteristics of the effects of all activity coefficients in the aqueous phase and the organic phase:

$$\left(\frac{[[\text{Activity Coefficients}]]_A}{[[\text{Activity Coefficients}]]_O} \right) =$$

$$A_0 + A_1 * (HNO_3)_{AT} ** A_2 + A_3 * (HNO_3)_{AT} ** A_4 \qquad (3.38)$$

With the concept of overall effects of all activity coefficients in the aqueous phase and in the organic phase, eliminate all terms in the activity coefficient in the equation (3.37) by using equation (3.38):

$$K_d = \frac{K_e * (NO_3^{-1})_A^{\,3} * (TBP)_O^{\,3}}{1 + K_1 * (NO_3^{-1})_A + K_2 * (NO_3^{-1})_A^{\,2}} \quad *$$

$$(A_0 + A_1 * (HNO_3)_{AT} ** A_2 + A_3 * (HNO_3)_{AT} ** A_4) \qquad (3.39)$$

where A_0, A_1, A_2, A_3 and A_4 are constants. As results of activity coefficient expression eliminations, the equation (3.37) is simplified considerably. Equation (3.39) is the final form of the rare earths distribution coefficient in the HNO_3-H_2O-TBP System, and was used in our liquid-liquid equilibrium model.

CHAPTER 4

EVALUATION OF MODEL PARAMETERS

4.1 Evaluation Of Model Parameters

Many equations have been developed in Chapter 3. These equations express the chemical reactions taking place in the aqueous phase, and in the organic phase, so mass can transfer from one phase to another. The chemical reaction equilibrium constants, the phase equilibrium constants and the effects of activity coefficients, both in the aqueous phase and organic phase, were all incorporated into those relationships.

The development of equations is just part of model construction. The ultimate goal is to construct a equilibrium model that will predict accurately the rare earths distribution in the HNO_3-H_2O-TBP system by using the relationships developed in Chapter 3.

We have developed the distribution model:

$$K_d = \frac{K_e*(NO_3^{-1})_A^{\ 3}*(TBP)_O^{\ 3}}{1 + K_1*(NO_3^{-1})_A + K_2*(NO_3^{-1})_A^{\ 2}} \quad *$$

$$(A_0 + A_1*(HNO_3)_{AT}**A_2 + A_3*(HNO_3)_{AT}**A_4) \qquad (3.39)$$

And the following nine simultaneous non-linear equations:

1.

$$(NO_3{}^{-1})_A = DOD*(HNO_3)_{AT} \tag{3.22}$$

2.

$$DOD = 1.0006204 - 0.020407*(HNO_3)_{AT} - 0.004496*((HNO_3)_{AT})**2 + 0.0001546*((HNO_3)_{AT})**3 \tag{3.21}$$

3.

$$((HNO_3)_n\text{-}TBP)_O = -0.07272 - 1.062423*(HNO_3)_{AT} - 0.173784*((HNO_3)_{AT})**2 + 0.0186665*((HNO_3)_{AT})**3 - 0.001062*((HNO_3)_{AT})**4 + 0.0000261*((HNO_3)_{AT})**5 \tag{3.15}$$

4.

$$(M(NO_3)_3(TBP)_3)_O = K_e*(M^{+3})_A*(NO_3{}^{-1})_A{}^3*(TBP)_O{}^3 \tag{3.2}$$

5.

$$(HNO_3)_{AI} = (1-DOD)*(HNO_3)_{AT} + (H^+)_A + (1/3)*(RRE)_{AI} + ((HNO_3)_n\text{-}TB)_O \tag{3.28}$$

6.

$$(RRE)_{AI} = (M^{+3})_A*(1 + K_e{}'*(NO_3{}^{-1})_A{}^3*(TBP)_O{}^3 + K_1{}'*(NO_3{}^{-1})_A + K_2{}'*(NO_3{}^{-1})_A{}^2) \tag{3.20}$$

7.

$$(HNO3)_{AI} = (HNO3)_{AT} + ((HNO_3)_n\text{-}TBP)_O + 3(M(NO_3)_3(TBP)_3)_O + (MNO_3{}^{+2})_A + 2(M(NO_3)_2{}^{+1})_A \tag{3.16}$$

8. $$(TBP)_{AI} = (TBP)_O + ((HNO_3)_n\text{-}TBP)_O/NOH + 3(M(NO_3)_3(TBP)_3)_O \qquad (3.17)$$

9. $$(TBP)_O = 3.428093 - 0.13173*(HNO_3)_{AT} + 0.028538*((HNO_3)_{AT})**2 - 0.003824 *((HNO_3)_{AT})**3 + 0.0002462*((HNO_3)_{AT})**4 - 0.000006359*((HNO_3)_{AT})**5 \qquad (3.30)$$

Eight model parameters:

K_e, K_1, K_2, A_0, A_1, A_2, A_3 and A_4

Nine unknowns in the simultaneous equations:

$(NO_3^{-1})_A$, $(TBP)_O$, $(HNO_3)_{AT}$, $((HNO_3)_n\text{-}TBP)_O$, $(H^+)_A$, $(M(NO_3)_3(TBP)_3)_O$, $(M^{+3})_A$, DOD and NOH

In addition, we have available experimental distribution coefficient data (K_d) for all 16 rare earth elements, over an acidity range of 0.3-16 M.

Based on the information we have summarized, it is now possible to evaluate the values of eight model parameters using a non-linear optimization technique. Mass balance for all chemical species involved in the HNO_3-H_2O-TBP two-phase system can be achieved simultaneously.

4.2 Procedures For Evaluating The Model Parameters

A computer program was developed to determine the eight equilibrium model parameters. The strategy is to solve the nine simultaneous non-linear equations, obtaining the mass balance relationships in this two-phase system, and then to minimize the difference between the model predicting and experimental distribution coefficient data K_d by adjusting the value of model parameters until converging criteria has been reached. IMSL's subroutine program DBCLSF (56) was incorporated into the following evaluation procedure.

Step 1. Give the value for $(HNO_3)_{AI}$, $(RRE)_{AI}$ and $(TBP)_{OI}$.

Step 2. Assign the initial value for model parameters

K_e, K_1, K_2, A_0, A_1, A_2, A_3 and A_4

Use published experimental data if available.

Step 3. Set the upper and lower bounds for 9 unknowns

$(NO_3^{-1})_A$, $(TBP)_O$, $(HNO_3)_{AT}$, $((HNO_3)_n\text{-}TBP)_O$, $(H^+)_A$, $(M(NO_3)_3(TBP)_3)_O$, $(M^{+3})_A$, DOD and NOH

For arithmetic purposes, the initial guess values for the above nine unknowns are required by IMSL's DBCLSF subprogram.

Step 4. Solve the simultaneous non-linear equations using the DBCLS subroutine, and obtain the calculated values for above nine unknown terms.

Step 5. Calculate the distribution coefficient through distribution model.

Step 6. Minimize the difference between the model predicting and experimental distribution coefficient data K_d, by adjusting the value of eight model parameters. IMSL subroutine program DBCLSF was called.

Step 7. Repeat Step 4 through Step 6 until the value of $(K_d)_{exp} - (K_d)_{calc}$ is less than tolerance.

4.3 Results

The value of the theoretical distribution model parameters for all 16 rare earth elements were listed in Table 4.1. Table 4.2 shows all 16 predicted distribution coefficients and their relative separation factors. The model predicts rare earths distribution coefficients accurately, with negligible deviations from the experimental data published by UK Harwell Laboratory. The verification of this theoretical model will be discussed in the next chapter. The source listing of the computer program for evaluating model parameters is attached in the Appendix C.

Table 4.1 The Parameters for the Distribution Model.

Elements	Ke	K1	K2	A0
Lutetium	3.7765E-03	6.0260E-01	1.5000E+01	9.8084E+00
Yttrium	1.6009E-04	6.0260E-01	1.5000E+01	4.2805E+02
Ytterbium	3.6319E-03	6.0260E-01	4.5017E+00	1.1246E+01
Thulium	4.4139E-03	7.0790E-01	1.2500E+01	8.2710E+00
Erbium	1.7464E-04	7.5000E-01	1.6105E+01	7.4199E+02
Holmium	4.8020E-02	7.5000E-01	1.0859E+01	1.7245E+00
Dysprosium	2.9289E-04	8.0000E-01	2.5000E+01	6.1135E+02
Terbium	7.3684E-03	1.1300E+00	3.5000E+01	3.0932E+01
Gadolinium	7.5454E-03	1.2500E+00	2.5000E+01	4.6249E+01
Europium	4.8544E-02	2.0400E+00	4.7091E+01	1.5713E+00
Samarium	9.1132E-04	3.2000E+00	3.5000E+01	3.0849E+02
Promethium	1.3855E-02	2.4800E+00	2.5000E+01	-7.2923E+00
Neodymium	1.0000E-01	8.0000E-01	9.0243E+00	-2.3811E-01
Praseodymium	1.0000E-01	1.6982E+00	3.2448E+01	-2.9400E+00
Cerium (III)	3.2647E-01	1.6300E+00	1.9114E+01	-2.2172E-01
Lanthanium	3.8348E-02	1.2882E+00	1.0765E+01	-2.1943E-01

Elements	A1	A2	A3	A4
Lutetium	2.7193E-01	3.7806E+00	6.1514E-09	1.1706E+01
Yttrium	6.4441E+00	3.0916E+00	8.9564E-06	9.8854E+00
Ytterbium	6.7744E-02	3.5478E+00	1.7513E-06	8.7219E+00
Thulium	1.9270E+00	1.9068E+00	1.0011E-05	8.2586E+00
Erbium	2.8451E+00	3.4183E+00	8.0252E-06	9.6484E+00
Holmium	2.1721E-03	3.3385E+00	4.4457E-06	7.2040E+00
Dysprosium	3.3406E-01	4.0502E+00	6.0624E-07	1.0478E+01
Terbium	2.3170E-01	2.3466E+00	4.2961E-07	9.2689E+00
Gadolinium	-2.2406E+01	1.2500E-01	3.5212E-06	7.9373E+00
Europium	6.9358E+00	-4.5006E-01	9.6604E-07	7.7463E+00
Samarium	-2.5754E+01	1.1617E+00	1.1257E-03	6.0768E+00
Promethium	2.3771E+01	-4.1865E-01	1.0932E-05	6.4171E+00
Neodymium	1.0176E+00	-5.4992E-01	3.3469E-07	6.3364E+00
Praseodymium	4.7418E+00	-2.3403E-01	6.0574E-05	4.4400E+00
Cerium (III)	5.3016E-01	-4.7404E-01	7.0708E-05	3.4566E+00
Lanthanium	1.3901E+00	-8.6901E-01	1.0670E-05	4.5425E+00

Table 4.2 The Predicted Distribution Coefficients and Separation Factors.

(HNO3)ai	0.1	0.2	0.5	0.7	1	1.5	2	2.5	3	3.5	4	4.5
(HNO3)at	0.08383	0.13	0.2722	0.37	0.521	0.784	1.06	1.35	1.66	1.97	2.3	2.64
(NO3-1)a	0.08373	0.1298	0.2708	0.367	0.515	0.771	1.03	1.3	1.58	1.86	2.14	2.42
(TBP)o	3.46	3.45	3.42	3.4	3.38	3.34	3.31	3.29	3.26	3.25	3.23	3.22
Lutecium	0.000782	0.0025	0.01302	0.02229	0.03695	0.06153	0.08701	0.1161	0.1532	0.2056	0.2841	0.4038
SF Lu/Y	0.540428	0.539956	0.540248	0.540494	0.540678	0.542592	0.549305	0.566065	0.598437	0.654985	0.742550	0.865038
Yttrium	0.001447	0.00463	0.0241	0.04124	0.06834	0.1134	0.1584	0.2051	0.256	0.3139	0.3826	0.4668
SF Y/Yb	1.571118	1.454602	1.107536	0.946088	0.795483	0.672597	0.618025	0.592090	0.580894	0.578297	0.581017	0.586505
Ytterbium	0.000921	0.003183	0.02176	0.04359	0.08591	0.1686	0.2563	0.3464	0.4407	0.5428	0.6585	0.7959
SF Yb/Tm	1.183804	1.258102	1.549857	1.741510	1.961415	2.120754	2.095666	1.976041	1.820322	1 661463	1.521487	1.410419
Thulium	0.000778	0.00253	0.01404	0.02503	0.0438	0.0795	0.1223	0.1753	0.2421	0.3267	0.4328	0.5643
SF Tm/Er	0.289326	0.296948	0.324699	0.341240	0.363184	0.400503	0.445050	0.499430	0.564598	0.639835	0.722778	0.809728
Erbium	0.002689	0.00852	0.04324	0.07335	0.1206	0.1985	0.2748	0.351	0.4288	0.5106	0.5988	0.6969
SF Er/Ho	1.515783	1.463917	1.312291	1.243641	1.180039	1.128482	1.106260	1.097560	1.096955	1.104238	1.119461	1.142833
Holmium	0.001774	0.00582	0.03295	0.05898	0.1022	0.1759	0.2484	0.3198	0.3909	0.4624	0.5349	0.6098
SF Ho/Dy	0.504407	0.551136	0.705416	0.787555	0.872013	0.948759	0.987281	1.009469	1.023834	1.033758	1.041269	1.047226
Dysprosium	0.003517	0.01056	0.04671	0.07489	0.1172	0.1854	0.2516	0.3168	0.3818	0.4473	0.5137	0.5823
SF Dy/Tb	0.847469	0.894157	0.997224	1.032395	1.059674	1.076655	1.080756	1.078651	1.073376	1.066777	1.058738	1.051652
Terbium	0.00415	0.01181	0.04684	0.07254	0.1106	0.1722	0.2328	0.2937	0.3557	0.4193	0.4852	0.5537
SF Tb/Gd	0.967591	0.953957	0.909691	0.899442	0.899918	0.9184	0.943273	0.971551	1.002536	1.036076	1.073213	1.114308
Gadolinium	0.004289	0.01238	0.05149	0.08065	0.1229	0.1875	0.2468	0.3023	0.3548	0.4047	0.4521	0.4969
SF Gd/Eu	0.238994	0.307960	0.475746	0.555249	0.643455	0.743457	0.814521	0.868927	0.913021	0.949554	0.980694	1.007706
Europium	0.017946	0.0402	0.10823	0.14525	0.191	0.2522	0.303	0.3479	0.3886	0.4262	0.461	0.4931
SF Eu/Sm	3.977393	3.210862	2.185581	1.875161	1.602348	1.362506	1.232208	1.154280	1.106177	1.078714	1.066389	1.066392
Samarium	0.004512	0.01252	0.04952	0.07746	0.1192	0.1851	0.2459	0.3014	0.3513	0.3951	0.4323	0.4624
SF Sm/Pm	0.308533	0.360599	0.467169	0.526580	0.608163	0.731620	0.843857	0.946013	1.039656	1.124359	1.200166	1.266849
Promathium	0.014624	0.03472	0.106	0.1471	0.196	0.253	0.2914	0.3186	0.3379	0.3514	0.3602	0.365
SF Pm/Nd	1.811245	1.679729	1.357929	1.245449	1.163204	1.119469	1.116903	1.128166	1.144260	1.162037	1.180596	1.199868
Neodymium	0.008074	0.02067	0.07806	0.11811	0.1685	0.226	0.2609	0.2824	0.2953	0.3024	0.3051	0.3042
SF Nd/Pr	0.819445	0.863048	1.079518	1.193150	1.299151	1.376370	1.403442	1.416959	1.428640	1.443436	1.463309	1.488986
Praseodymium	0.009853	0.02395	0.07231	0.09899	0.1297	0.1642	0.1859	0.1993	0.2067	0.2095	0.2085	0.2043
SF Pr/Ce	1.050874	1.066340	1.040581	1.034054	1.041767	1.076015	1.117859	1.161421	1.205247	1.250746	1.297448	1.344963
Cerium (III)	0.009376	0.02246	0.06949	0.09573	0.1245	0.1526	0.1663	0.1716	0.1715	0.1675	0.1607	0.1519
SF Ce/La	1.007630	1.102601	1.191733	1.215464	1.249749	1.307626	1.360883	1.403107	1.436348	1.460331	1.474311	1.481951
Lanthanum	0.009305	0.02037	0.05831	0.07876	0.09962	0.1167	0.1222	0.1223	0.1194	0.1147	0.109	0.1025

Table 4.2 The Predicted Distribution Coefficients and Separation Factors (Continued).

(HNO3)ai	5	5.5	6	6.5	7	7.5	8	8.5	9	9.5	10	11
(HNO3)at	2.99	3.34	3.71	4.08	4.49	4.85	5.24	5.64	6.04	6.44	6.85	7.66
(NO3-1)a	2.7	2.97	3.23	3.48	3.72	3.95	4.15	4.34	4.51	4.66	4.79	4.98
(TBP)o	3.21	3.19	3.18	3.17	3.16	3.15	3.16	3.12	3.11	3.09	3.08	3.05
Lutecium	0.5852	0.8549	1.2454	1.796	2.5523	3.5667	4.9004	6.6269	8.8407	11.673	15.318	26.394
SF Lu/Y	1.022719	1.211936	1.423639	1.646799	1.867764	2.071013	2.239568	2.355561	2.404389	2.379767	2.288215	1.988398
Yttrium	0.5722	0.7054	0.8748	1.0906	1.3665	1.7222	2.1881	2.8133	3.6769	4.9051	6.6943	13.274
SF Y/Yb	0.592646	0.597189	0.598767	0.596543	0.590586	0.581843	0.572082	0.563663	0.559130	0.560896	0.570796	0.617596
Ytterbium	0.9655	1.1812	1.461	1.8282	2.3138	2.9599	3.8248	4.9911	6.5761	8.7451	11.728	21.493
SF Yb/Tm	1.331173	1.283355	1.264606	1.270907	1.297045	1.336539	1.381692	1.423994	1.455823	1.472214	1.472257	1.436986
Thulium	0.7253	0.9204	1.1553	1.4385	1.7839	2.2146	2.7682	3.505	4.5171	5.9401	7.966	14.957
SF Tm/Er	0.896095	0.977277	1.049318	1.110039	1.160109	1.202410	1.241289	1.281676	1.326880	1.377414	1.430392	1.520406
Erbium	0.8094	0.9418	1.101	1.2959	1.5377	1.8418	2.2301	2.7347	3.4043	4.3125	5.5691	9.8375
SF Er/Ho	1.175428	1.216010	1.261891	1.308197	1.346497	1.367944	1.365646	1.338112	1.291513	1.237091	1.186783	1.131696
Holmium	0.6886	0.7745	0.8725	0.9906	1.142	1.3464	1.633	2.0437	2.6359	3.486	4.6926	8.6927
SF Ho/Dy	1.052583	1.058783	1.067931	1.082978	1.109060	1.151359	1.214577	1.300973	1.407539	1.524001	1.633401	1.756881
Dysprosium	0.6542	0.7315	0.817	0.9147	1.0297	1.1694	1.3445	1.5709	1.8727	2.2874	2.8729	4.9478
SF Dy/Tb	1.046385	1.044701	1.048242	1.058803	1.077317	1.104457	1.139503	1.180329	1.222708	1.261596	1.292352	1.325208
Terbium	0.6252	0.7002	0.7794	0.8639	0.9558	1.0588	1.1799	1.3309	1.5316	1.8131	2.223	3.7336
SF Tb/Gd	1.160141	1.210790	1.266699	1.327035	1.390456	1.453996	1.513080	1.562272	1.596414	1.614227	1.620026	1.630393
Gadolinium	0.5389	0.5783	0.6153	0.651	0.6874	0.7282	0.7798	0.8519	0.9594	1.1232	1.3722	2.29
SF Gd/Eu	1.030992	1.051837	1.070459	1.088082	1.105322	1.123938	1.145922	1.173415	1.208921	1.253012	1.304496	1.414453
Europium	0.5227	0.5498	0.5748	0.5983	0.6219	0.6479	0.6805	0.726	0.7936	0.8964	1.0519	1.619
SF Eu/Sm	1.077731	1.098721	1.129494	1.168782	1.215598	1.267162	1.320077	1.369036	1.408340	1.436078	1.454306	1.488735
Samarium	0.485	0.5004	0.5089	0.5119	0.5116	0.5113	0.5155	0.5303	0.5635	0.6242	0.7233	1.0875
SF Sm/Pm	1.323328	1.370208	1.406967	1.434295	1.453822	1.467987	1.481321	1.499293	1.528342	1.571896	1.629788	1.765708
Promethium	0.3665	0.3652	0.3617	0.3569	0.3519	0.3483	0.348	0.3537	0.3687	0.3971	0.4438	0.6159
SF Pm/Nd	1.219633	1.240067	1.261157	1.284274	1.310614	1.341162	1.378217	1.423913	1.479534	1.544535	1.616168	1.757203
Neodymium	0.3005	0.2945	0.2868	0.2779	0.2685	0.2597	0.2525	0.2484	0.2492	0.2571	0.2746	0.3505
SF Nd/Pr	1.520748	1.558201	1.600446	1.644378	1.687617	1.723291	1.744989	1.745607	1.724567	1.684796	1.637447	1.575280
Praseodymium	0.1976	0.189	0.1792	0.169	0.1591	0.1507	0.1447	0.1423	0.1445	0.1526	0.1677	0.2225
SF Pr/Ce	1.393511	1.443850	1.493333	1.540565	1.581510	1.611420	1.626390	1.624243	1.605733	1.580364	1.557103	1.541926
Cerium (III)	0.1418	0.1309	0.12	0.1097	0.1006	0.09352	0.08897	0.08761	0.08999	0.09656	0.1077	0.1443
SF Ce/La	1.482333	1.478427	1.474201	1.473472	1.481154	1.506928	1.556780	1.639101	1.755559	1.898171	2.049866	2.289022
Lanthanum	0.09566	0.08854	0.0814	0.07445	0.06792	0.06206	0.05715	0.05345	0.05126	0.05087	0.05254	0.06304

Table 4.2 The Predicted Distribution Coefficients and Separation Factors (Continued).

(HNO3)ai	12	13	14	15	16	17	18
(HNO3)at	8.48	9.29	10.1	10.89	11.68	12.45	13.22
(NO3-1)a	5.07	5.08	5	4.84	4.62	4.33	4
(TBP)o	3.02	2.99	2.96	2.93	2.89	2.84	2.77
Lutecium	46.903	87.442	168.77	326.64	614.45	1098.4	1837.2
SF Lu/Y	1.695636	1.517221	1.458308	1.487431	1.574866	1.700388	1.852016
Yttrium	27.661	57.633	115.73	219.6	390.16	645.97	992
SF Y/Yb	0.696312	0.795607	0.904706	1.016807	1.128706	1.239603	1.350100
Ytterbium	39.725	72.439	127.92	215.97	345.67	521.11	734.76
SF Yb/Tm	1.386803	1.347276	1.325115	1.318015	1.321520	1.331842	1.346108
Thulium	28.645	53.767	96.535	163.86	261.57	391.27	545.84
SF Tm/Er	1.554934	1.525954	1.454015	1.363001	1.268341	1.177779	1.094108
Erbium	18.422	35.235	66.392	120.22	206.23	332.21	498.89
SF Er/Ho	1.156797	1.256866	1.418026	1.628114	1.878746	2.164939	2.484759
Holmium	15.925	28.034	46.82	73.84	109.77	153.45	200.78
SF Ho/Dy	1.694816	1.496982	1.257520	1.034622	0.847972	0.697848	0.578233
Dysprosium	9.3963	18.727	37.232	71.369	129.45	219.89	347.23
SF Dy/Tb	1.342597	1.375498	1.433411	1.512394	1.606041	1.709211	1.819291
Terbium	6.9986	13.6147	25.9744	47.1894	80.6019	128.65	190.86
SF Tb/Gd	1.684785	1.792658	1.938532	2.107610	2.290412	2.482105	2.680354
Gadolinium	4.154	7.5947	13.399	22.39	35.191	51.831	71.207
SF Gd/Eu	1.508406	1.576972	1.625894	1.662459	1.691712	1.716485	1.738197
Europium	2.7539	4.816	8.241	13.468	20.802	30.196	40.966
SF Eu/Sm	1.559399	1.676529	1.830845	2.011740	2.212155	2.427916	2.657541
Samarium	1.766	2.8726	4.5012	6.6947	9.4035	12.437	15.415
SF Sm/Pm	1.881926	1.953352	1.985881	1.992944	1.985200	1.969188	1.948700
Promethium	0.9384	1.4706	2.2666	3.3592	4.7368	6.3158	7.9104
SF Pm/Nd	1.862643	1.926634	1.962594	1.984170	1.998902	2.010568	2.020846
Neodymium	0.5038	0.7633	1.1549	1.693	2.3697	3.1413	3.9144
SF Nd/Pr	1.599365	1.704555	1.866655	2.065893	2.290893	2.535146	2.795600
Praseodymium	0.315	0.4478	0.6187	0.8195	1.0344	1.2391	1.4002
SF Pr/Ce	1.574212	1.639692	1.723878	1.817476	1.915910	2.016764	2.119588
Cerium (III)	0.2001	0.2731	0.3589	0.4509	0.5399	0.6144	0.6606
SF Ce/La	2.373665	2.336184	2.237531	2.122881	2.007809	1.900990	1.802947
Lanthanum	0.0843	0.1169	0.1604	0.2124	0.2689	0.3232	0.3664

Table 4.2 The Predicted Distribution Coefficients and Separation Factors (Continued).

CHAPTER 5

VERIFICATION OF THE THEORETICAL MODEL

5.1 Verification By Experimental Data

Verification is a necessary step to certify the correctness and accuracy for any kind of mathematical model. Only after certification, can the model be used with confidence. Comparing the experimental and model predicted data in different cases is one of the easiest methods to verify models. Tables 5.1 to 5.16 summarize the experimental and the predicted distribution coefficients, component concentrations in the aqueous phase and the organic phase for all 16 rare earth elements. The nitric acid degree of dissociation with different aqueous acidities was also shown in these tables. Figures 5.1 to 5.16 present the experimental and model predicted distribution coefficients graphically for all 16 elements. Figures 5.17 to 5.32 compare the published and model predicted data in a bar chart form versus the natural logarithm scale of K_d. The natural logarithm scale is a more distinct way to show the differences between the experimental data and the model predicted data. Table 5.1, Figure 5.1 and Figure 5.17, which are located in the following pages, shows the comparison of the experimental and model predicted distribution coefficients and the equilibrium concentrations for lutetium, a representative

Table 5.1 The Calculated Distribution Coefficients of Lutetium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.52	0.0133	0.0134	0.2785	1.660000E-05	0.9948	0.2769
2	1.03	0.0340	0.0399	0.5550	5.616000E-04	0.9879	0.5483
3	1.56	0.0600	0.0669	0.8417	3.977000E-04	0.9804	0.8251
4	2.17	0.0750	0.0998	1.1873	3.471000E-04	0.9703	1.1521
5	3.23	0.1980	0.1809	1.8283	2.091000E-04	0.9492	1.7355
6	4.36	0.4400	0.3764	2.5676	1.425000E-04	0.9212	2.3652
7	4.73	0.6300	0.4920	2.8215	1.548000E-04	0.9107	2.5696
8	5.38	0.9600	0.7985	3.2790	1.760000E-04	0.8907	2.9207
9	6.16	1.4800	1.4258	3.8479	2.003000E-04	0.8641	3.3248
10	7.35	3.1000	3.2655	4.7507	2.341000E-04	0.8181	3.8862
11	9.03	8.6000	9.0446	6.0760	2.722000E-04	0.7436	4.5177
12	10.80	24.0000	23.6909	7.5071	2.969000E-04	0.6565	4.9277
13	12.80	77.0000	76.8910	9.1360	3.043000E-04	0.5528	5.0500
14	14.40	220.0000	220.1889	10.4276	2.954000E-04	0.4701	4.9021
15	15.50	450.0000	449.9329	11.2980	2.827000E-04	0.4154	4.6923

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.2993	0.0001	0.2159	0.0100	1.150100E-04	3.4038	1.0000
2	0.5536	0.0017	0.4665	0.0001	7.666130E-03	3.3631	1.5730
3	0.8311	0.0008	0.7090	0.0001	8.169480E-03	3.3353	2.1854
4	1.1585	0.0005	0.9729	0.0001	9.955000E-03	3.3060	2.7507
5	1.7423	0.0002	1.3916	0.0001	9.035880E-03	3.2619	3.4993
6	2.3722	0.0001	1.7822	0.0001	8.391250E-03	3.2233	4.0860
7	2.5766	0.0001	1.8981	0.0001	9.904260E-03	3.2122	4.2413
8	2.9306	0.0001	2.0877	0.0002	1.279573E-02	3.1942	4.4851
9	3.3386	0.0001	2.2950	0.0001	1.658144E-02	3.1745	4.7300
10	3.9062	0.0001	2.5761	0.0001	2.265382E-02	3.1464	5.0184
11	4.5459	0.0001	2.9228	0.0001	3.061441E-02	3.1064	5.2823
12	4.9618	0.0001	3.2558	0.0001	3.642334E-02	3.0600	5.4289
13	5.0859	0.0001	3.6252	0.0001	3.825375E-02	3.0010	5.5038
14	4.9357	0.0001	3.9358	0.0001	3.604587E-02	2.9486	5.5349
15	4.7229	0.0001	4.1685	0.0001	3.302651E-02	2.9086	5.5502

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

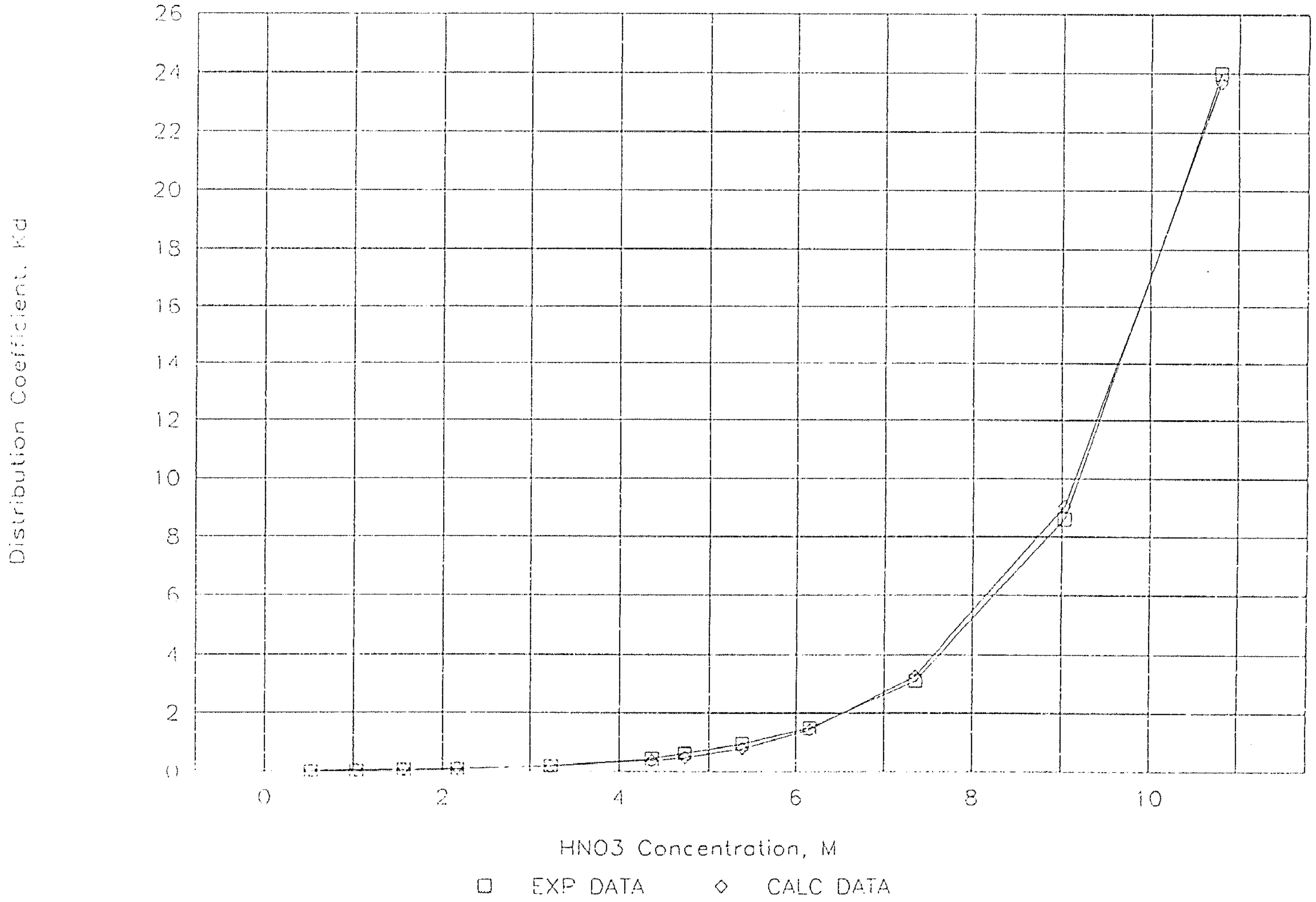

Figure 5.1 Comparison of the Experimental and Predicted Distribution Coefficients of Lutetium.

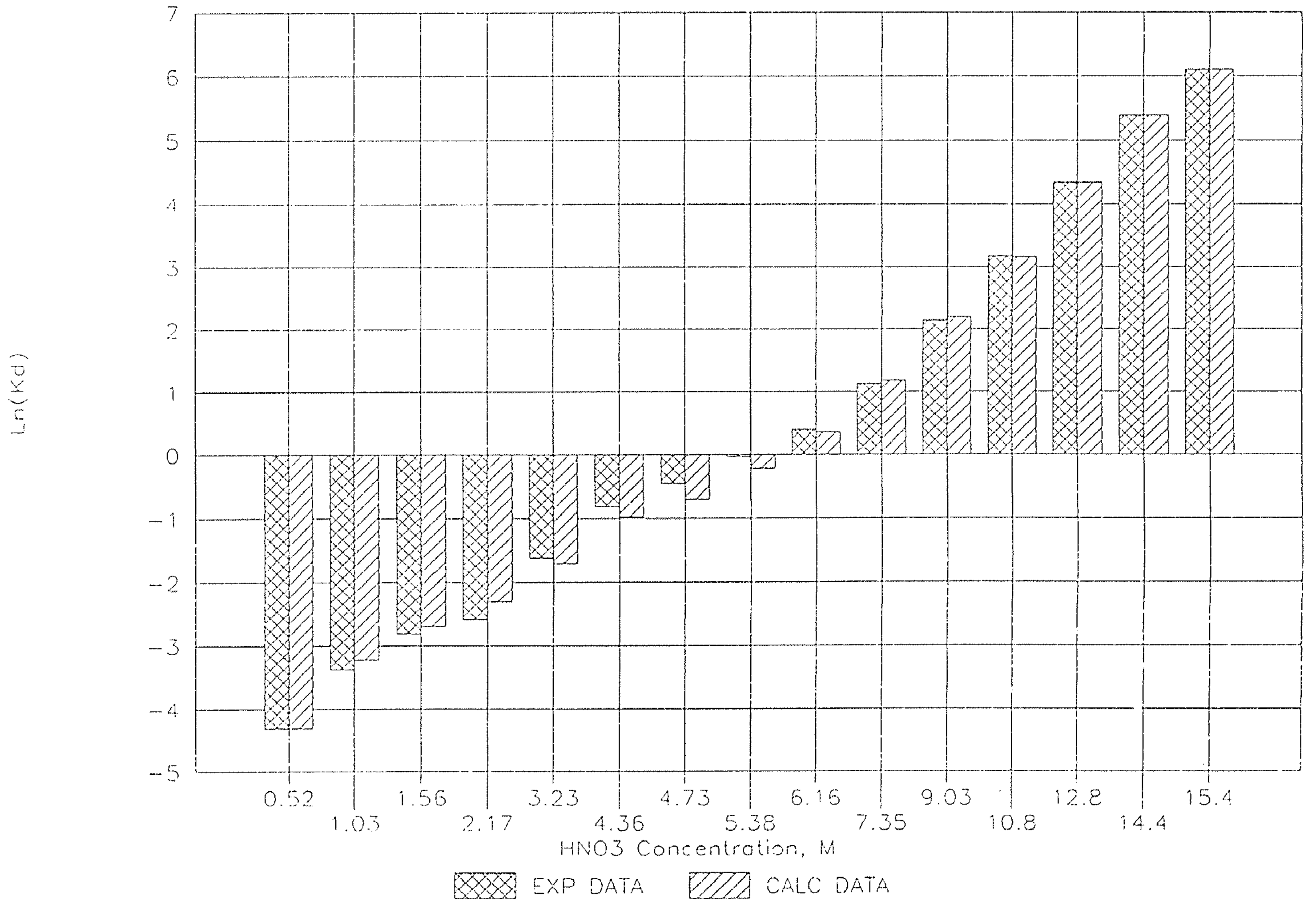

Figure 5.17 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Lutetium.

example for all 16 elements. The remaining cases are summarized in Appendices A and B.

5.2 Verification By Process Simulation

Verification of a model can be accomplished by practical model applications as well. Weaver and Kappelmann (57) of Oak Ridge National Laboratory developed a process for separating promethium from mixed fission product rare earths, by center-feed continuous multistage countercurrent extraction with 100% tri-n-butyl phosphate (TBP) from nitric acid of 12 N or higher concentration. A flowsheet for purification of promethium includes one cycle for separation of promethium from neodymium and lighter elements and a second cycle for removal of samarium and heavier elements. Each cycle consists of a series of countercurrent contact stages, followed by stripping stages and an evaporator. With 20 stages in the first cycle and 34 stages in the second, a 90% yield of promethium with a purity of 83% can be obtained, assuming a 100% stage efficiency. An increase to 25 stages in the first cycle would permit a 90% yield of 93% promethium. When the stages in the first cycle increased to 34, the promethium yield and purity increased to 93% and 99%, respectively.

The following are the important process parameters for Weaver and Kappelmann's flow sheet of the center-feed continuous multistage countercurrent extractor in the first cycle:

Number of Stages: 20 to 34 stages.

Feed: 0.5 l/h of 12.5 N HNO_3 solution, with 12.5 g of rare earths with composition (wt %):

Component	Wt %	Component	Wt %
La_2O_3	0.1421	Pr_2O_3	0.1421
Nd_2O_3	0.5372	Pm_2O_3	0.0630
Sm_2O_3	0.1080	Eu_2O_3	0.0036
Gd_2O_3	0.0007	Y_2O_3	0.0033

Extractant: 24.4 l/h of TBP, pre-equilibrated with 12 N HNO_3.

Scrub Solution: 14.5 l/h of 12 N HNO_3 solution.

We conducted several process simulations with stage numbers 20, 25 and 34 for the continuous multistage countercurrent extraction in the first cycle, with the Weaver and Kappelmann's process parameters. The theoretical equilibrium model developed by this research was used to predict the rare earths distribution in the HNO_3-H_2O-TBP system. The following is a comparison of promethium recovery from Weaver and Kappelmann's experiments with our simulations:

Promethium Recovery

	15 Stages	20 Stages	25 Stages	34 Stages
Weaver & Kappelmann	n/a	0.9000	0.9000	0.9524
This Work	0.9311	0.9989	0.9997	0.9999

The differences between the laboratory data obtained by Weaver and Kappelmann and our simulation results were caused by stage efficiencies. With limited data, the stage efficiency for Weaver and Kappelmann's extraction apparatus was estimated around 60-70%, while a 100% efficiency was used for all process simulations. Weaver and Kappelmann reported 90% recovery rate for both 20 stage and 25 stage cases. We doubt the accuracies of Weaver and Kappelmann's experiments, because their results are contrary to the principle of equilibrium stage operation. Generally, if same stage efficiency was used, and same acid strength was maintained, the recovery rate of a specific specie increases in accordance with the increasing of the number of contact stages.

Weaver and Kappelmann suggested that operation at higher acidity is possible with relative flow rates different with a smaller organic flow. We decided to verify this statement by extracting promethium from mixed fission product rare earths with center-feed extractor, stage numbers from 20 to 60, and with three acidities 11 N, 12 N, and 13 N. We have found that in lower acidity, relative higher organic flow rates were required, on the contrary, with higher acidities, relative lower organic flow rate would be enough. In general, a higher organic flow rate and a higher number of stages will have positive effects on promethium recovery. The results of investigation are shown in details in Tables 5.17 to 5.19 and Figures 5.33 to 5.35.

Table 5.17 and Figure 5.33 are located in the following pages, the remaining tables and figures are placed in Appendices A and B, respectively.

5.3 Computer Program For Liquid-Liquid Extraction Computation

A computer program was developed for the calculations of multicomponent, multistage, counter-current liquid-liquid extraction operations. The Isothermal Sum-Rates (ISR) algorithm which was presented by Tsuboka and Katayama (67) was chosen for its simplicity and numerical reliability, even though the ISR algorithm is slow in convergence compared to other algorithms such as the Newton-Raphson method proposed by Roche (58), (59), and Naphtali and Sandholm (60). Details on the ISR algorithm can be found from Henley and Seader (61). Some modifications were made on the ISR to adapt it to our needs. The program source listing and input file are attached in Appendix D.

5.4 Conclusion

Based on the above discussions, the theoretical model developed by this research accurately predicts the rare earths distribution coefficients in the HNO_3-H_2O-TBP system. Therefore, we have confidence that this model can be used to predict the rare earth distribution in the HNO_3-H_2O-TBP system under any circumstances.

Table 5.17 The Effect of Number of Stages on Promethium Extraction, HNO_3 11.0 N.

	% OF PROMETHIUM EXTRACTED		
STAGE	CASE A	CASE B	CASE C
20	79,1367	84,5151	88,5961
25	82,1801	87,7845	91,6906
30	87,1867	92,1245	95,1901
35	89,4500	94,0271	96,6271
40	92,5172	96,2099	98,0773
45	93,9694	97,1814	98,6734
50	95,7633	98,2268	99,2488
55	96,6277	98,6939	99,4851
60	97,6449	99,1820	99,7093

Feed 11.0 N HNO_3 0.5 l/h, center feed
Rare Earth in feed 25.0 g/l
Solvent TBP equilibrated with 11.0 N HNO_3
case a: 25.40 l/h
case b: 26.28 l/h
case c: 27.15 l/h
Scrub 11.0 N HNO_3, 14.5 l/h

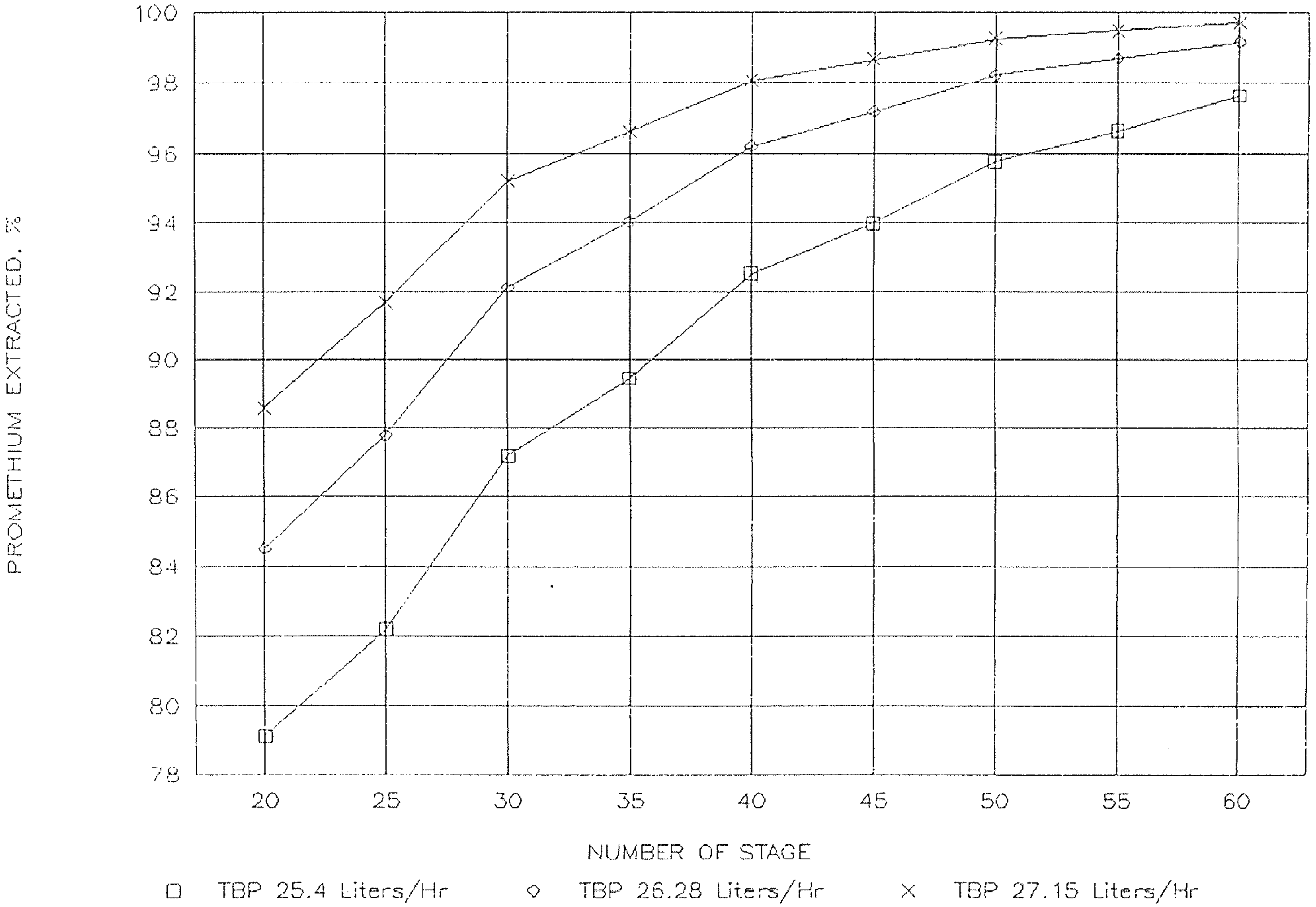

Figure 5.33 The Effect of Number of Stages on Promethium Extraction HNO_3 11.0 N.

CHAPTER 6

SEPARATION OF EUROPIUM
FROM
JIANGXI MINERAL SAMPLE

6.1 The Design Basis For Separation And Purification

A lanthanide and yttrium mineral sample in the form of oxides was taken from Jiangxi Province, China (79) having the following composition (wt %):

Component	Wt %	Component	Wt %
Lu_2O_3	0.07675	Y_2O_3	7.6765
Yb_2O_3	0.5118	Tm_2O_3	0.07675
Er_2O_3	0.7677	Ho_2O_3	0.1024
Dy_2O_3	1.7912	Tb_2O_3	0.4094
Gd_2O_3	3.5824	Eu_2O_3	0.5630
Sm_2O_3	4.6060	Nd_2O_3	29.6827
Pr_2O_3	8.7001	Ce_2O_3	2.5588
La_2O_3	38.8945		

It was decided to separate the contents of the Jiangxi mineral sample into two or three sub-groups and later on certain specific rare earths in the sub-group can be separated and purified to purity 99.9% or higher for market needs by the liquid-liquid extraction process in the HNO_3-H_2O-TBP system. The rare earth distributions in the aqueous phase and in the organic phase will be predicted by the theoretical model developed by this research.

6.2 Separation Of The Sub-Group Lu-Tb From Jiangxi Mineral Sample

The lanthanide and yttrium oxides mineral sample taken from Jiangxi, China was separated into two sub-groups Lu-Tb and Gd-La by a center-feed, multistage counter-current extractor. A 100% stage efficiency was used. The important process parameters we found are listed below. Those parameters are similar to Korpusov et al. (62) lanthanide and yttrium separation experience, but not identical.

Number of Stages: 34 to 65 stages

Feed: 8.2 N HNO_3, 1.0 l/h, with rare earths and yttrium 265.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 8.2 N HNO_3, 3.5 l/h.

Scrub Solution : 8.2 N HNO_3, 2.0 l/h.

The effect of the number of stages on the extraction of sub-group Lu-Tb was studied. Initially, 34 contact stages were used in the extraction device, resulting in 93.40% of terbium extracted by the TBP organic solution. However, when the number of stages increased to 65, 98.39% of terbium will be transferred to the organic phase from the aqueous phase by extraction. Higher extractabilities were reported for yttrium and elements heavier than terbium in both cases.

Calculation results were tabulated in Table 6.1 and plotted in Figure 6.1.

6.3 Separation Of The Sub-Group Lu-Sm From Jiangxi Mineral Sample

The separation of the sub-group Lu-Sm from Jiangxi lanthanide and yttrium oxides sample was also investigated. The reasons for samarium was chosen as a cut point in separation is because samarium has low economic value (70); higher percentage in composition; and large separation factor relative to neodymium. Here are the process parameters:

Number of Stages: 20 to 28 stages

Feed: 10.0 N HNO_3, 1.0 l/h, with rare earths and yttrium 160.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 10.0 N HNO_3, 6.0 l/h.

Scrub Solution: 10.0 N HNO_3, 2.0 l/h.

After process model simulation, we found that 98.76% of Samarium is extracted into the organic phase by a 20 contact stages extractor. When the contact stage increases to 28, the extraction rate for samarium increases to 99.70% accordingly. Results from this study were also summarized in Table 6.2 and plotted in Figure 6.2.

Table 6.1 The Effect of Number of Stages on the Separation of Sub-group Lu-Tb from Jiangxi Mineral Sample.

RARE EARTH COMPONENTS EXTRACTED, %

COMPONENT	NUMBER OF STAGE							
	34	35	40	45	50	55	60	65
Lu	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Y	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Yb	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Tm	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Er	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Ho	99.9999	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000	100.0000
Dy	99.9147	99.9149	99.9711	99.9860	99.9960	99.9981	99.9994	99.9997
Tb	93.3980	93.4077	94.9490	95.7482	97.0813	97.5467	98.0942	98.3876
Gd	6.4211	5.9011	5.0177	3.9768	3.8844	3.1820	2.7969	2.3145
Eu	0.0213	0.0135	0.0055	0.0014	0.0007	0.0002	0.0000	0.0000
Sm	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Nd	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Pr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ce(III)	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
La	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Feed 8.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 265.0 g/l
Solvent TBP 3.5 l/h, equilibrated with 8.2 N HNO_3
Scrub 8.2 N HNO_3, 2.0 l/h

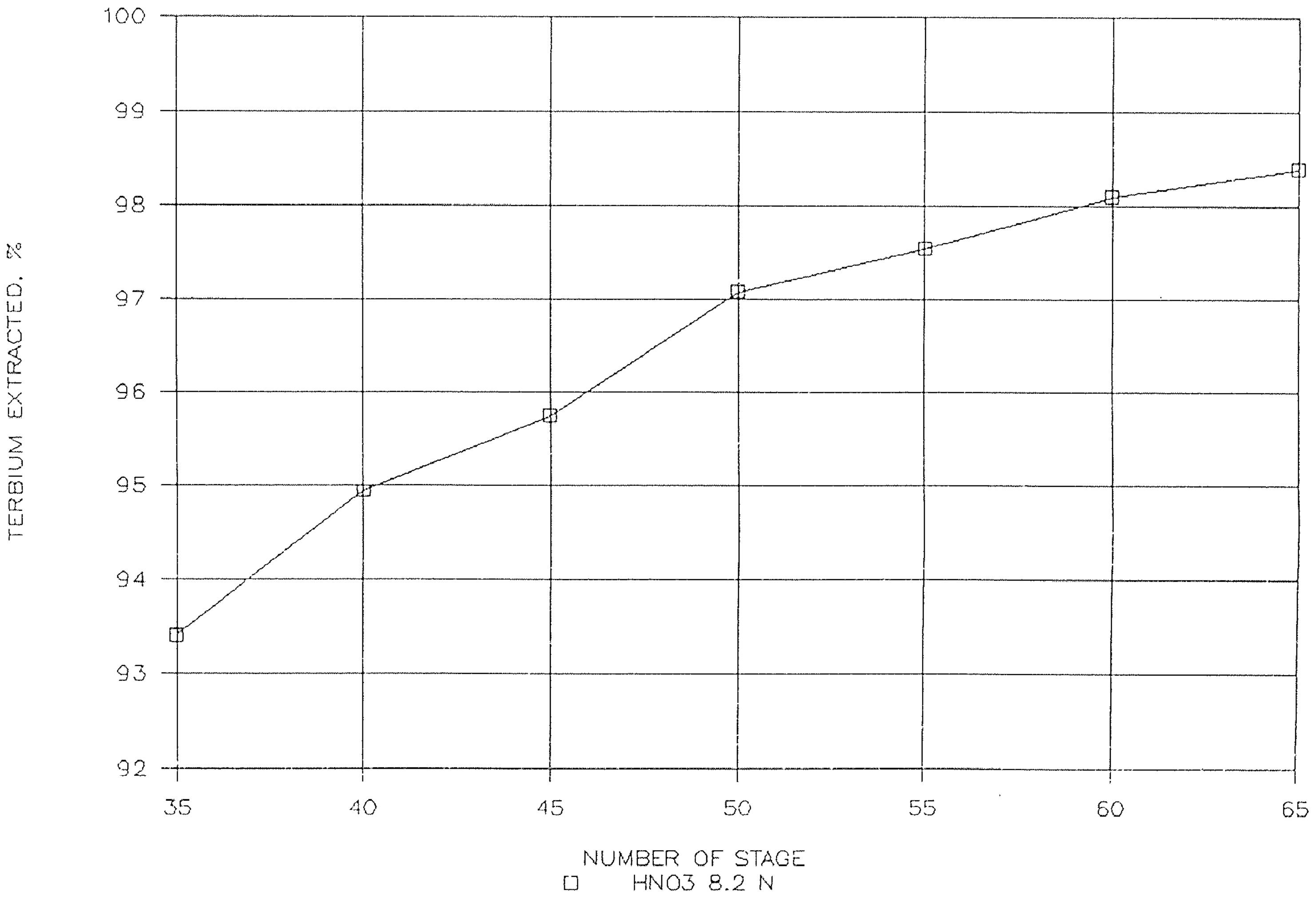

Figure 6.1 The Effect of Number of Stages on the Separation of Sub-group Lu-Tb from Jiangxi Mineral Sample.

Table 6.2 The Effect of Number of Stages on the Separation of Sub-group Lu-Sm from Jiangxi Mineral Sample.

RARE EARTH COMPONENTS EXTRACTED, %

COMP	NUMBER OF STAGE				
	20	22	24	26	28
Lu	100,0000	100,0000	100,0000	100,0000	100,0000
Y	100,0000	100,0000	100,0000	100,0000	100,0000
Yb	100,0000	100,0000	100,0000	100,0000	100,0000
Tm	100,0000	100,0000	100,0000	100,0000	100,0000
Er	100,0000	100,0000	100,0000	100,0000	100,0000
Ho	99,9999	100,0000	100,0000	100,0000	100,0000
Dy	100,0000	100,0000	100,0000	100,0000	100,0000
Tb	100,0000	100,0000	100,0000	100,0000	100,0000
Gd	99,9999	100,0000	100,0000	100,0000	100,0000
Eu	99,9968	99,9988	99,9995	99,9998	99,9999
Sm	98,7629	99,1301	99,3876	99,5686	99,6959
Nd	0,1699	0,0980	0,0566	0,0326	0,0188
Pr	0,0005	0,0002	0,0000	0,0000	0,0000
Ce(III)	0,0000	0,0000	0,0000	0,0000	0,0000
La	0,0000	0,0000	0,0000	0,0000	0,0000

Feed 10.0 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 160.0 g/l
Solvent TBP 6.0 l/h, equilibrated with 10.0 N HNO_3
Scrub 10.0 N HNO_3, 2.0 l/h

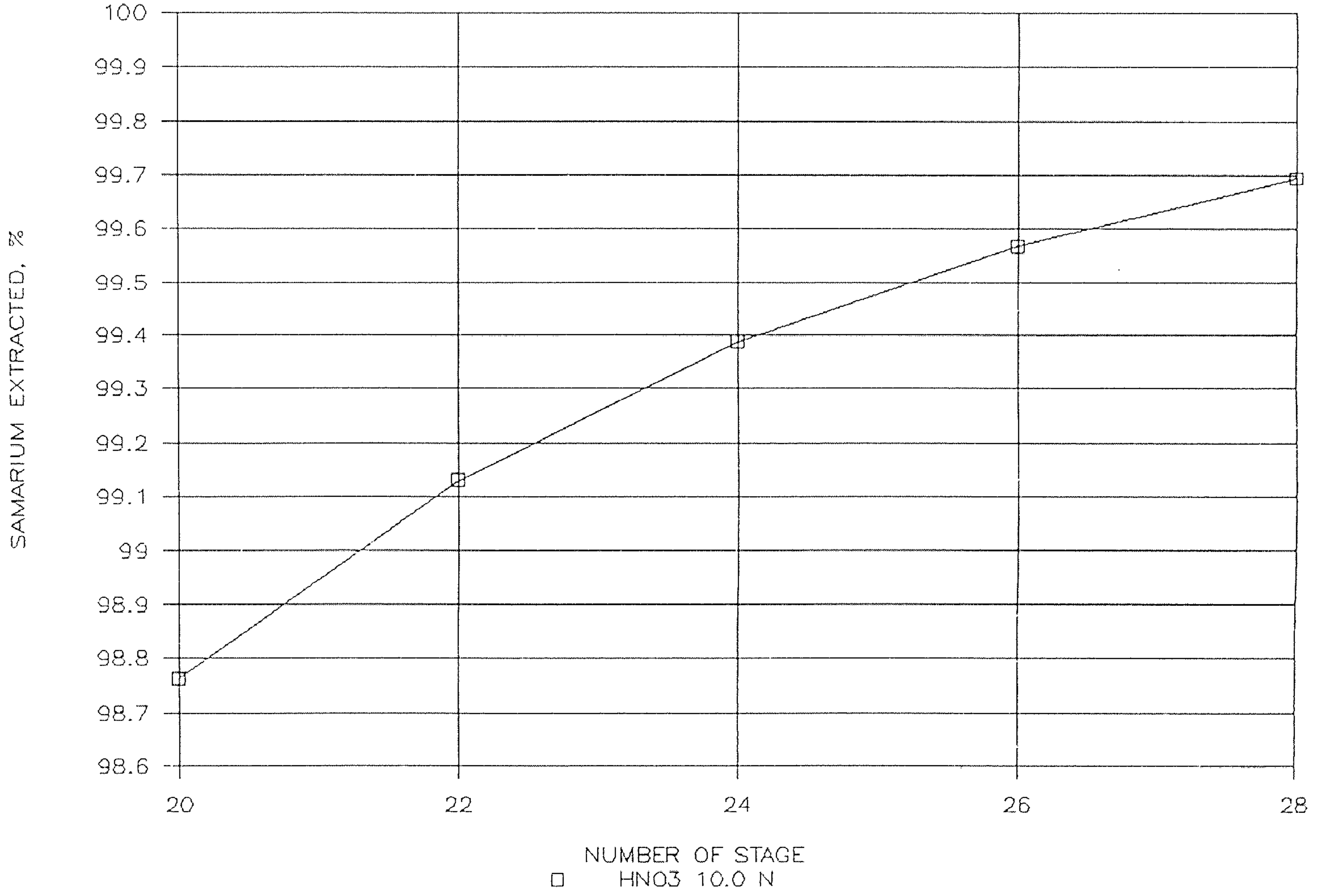

Figure 6.2 The Effect of Number of Stages on the Separation of Sub-group Lu-Sm from Jiangxi Mineral Sample.

Based on the experience gained by separating the sub-groups Lu-Sm and Lu-Tb from the Jiangxi rare earths mineral sample, the conclusion we draw is that the number of stages in an extraction operation has a positive impact on the cleanness of separation; i.e., the higher the number of stages used in the separation process, the cleaner the products are that can be obtained.

6.4 Separation Of Gadolinium From The Sub-Group Gd-La Of Jiangxi Mineral Sample

It was decided to separate gadolinium from the sub-group Gd-La of the lanthanide and yttrium oxides mineral sample which was taken from Jiangxi, China by extraction process, so europium can be sequentially separated from the remaining sub-group Eu-La exists in the aqueous phase and then be further processed to higher purity, or higher value commodity. The sub-group Gd-La which is the feed of this separation process, as a matter of fact, are the species remain unextracted and exist in the raffinate stream of the separation process which was discussed in Section 6.2, has the following composition (wt %):

Component	**Wt %**	**Component**	**Wt %**
Gd_2O_3	4.0439	Eu_2O_3	0.6355
Sm_2O_3	5.1994	Nd_2O_3	33.5066
Pr_2O_3	9.8209	Ce_2O_3	2.8884
La_2O_3	43.9052		

A 100% stage efficiency was assumed. The optimum process parameters for separating gadolinium from the sub-group Gd-La are listed below:

Number of Stages: 66 to 120 stages.

Feed: 9.5 N HNO_3, 1.0 l/h, with rare earths 133 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.5 N HNO_3, 1.9 l/h.

Scrub Solution : 9.5 N HNO_3, 2.0 l/h.

Because gadolinium has smaller separation factor (1.5 - 1.6) relative to europium, comparing to the separation factors of Sm/Nd (3.1 - 3.5) in Section 6.2 and Tb/Gd (1.8 - 1.9) in Section 6.3, the clean-cut separation of gadolinium from the sub-group Gd-La is rather difficulty, even with large stage numbers. For example, in above GD9519 case, initially 66 contact stages were used, 0.3678% of europium was extracted by the TBP extractant. As the stage number increased to 120, the europium extraction rate decreased to 0.0153%, i.e., 99.9847% of europium remained in the aqueous phase, therefore, 99.99% or higher purity of gadolinium was produced. However, the recovery rates for gadolinium were only 77.23 - 78.65 %. Simulation results were tabulated in Table 6.3 and plotted in Figure 6.3.

Table 6.3 The Effect of Number of Stages on the Separation of Gd from the Sub-group Gd-La, Gd Extracted %.

	CASE NUMBERS					
STAGE	GD9029	GD9031	GD9035	GD9519	GD9520	GD9522
66	84.7843	94.7356	99.7235	77.2364	87.6784	97.9363
72	85.2711	95.2944	99.8166	77.5584	88.2277	98.3146
80	85.8015	95.9126	99.8937	77.8878	88.8371	98.7048
88	86.2284	96.4196	99.9384	78.1333	89.3384	98.9985
86	86.5765	96.8415	99.9642	78.3179	89.7569	99.2219
104	86.8635	97.1968	99.9792	78.4577	90.1106	99.3931
112	87.1023	97.4993	99.9879	78.5641	90.4126	99.5252
120	87.3025	97.7589	99.9930	78.6456	90.6730	99.6276

Feed 9.0-9.5 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 132.88 g/l
Solvent TBP 2.1 l/h, equilibrated with 9.0-9.5 N HNO_3
Scrub 9.0-9.5 N HNO_3, 1.9-3.5 l/h

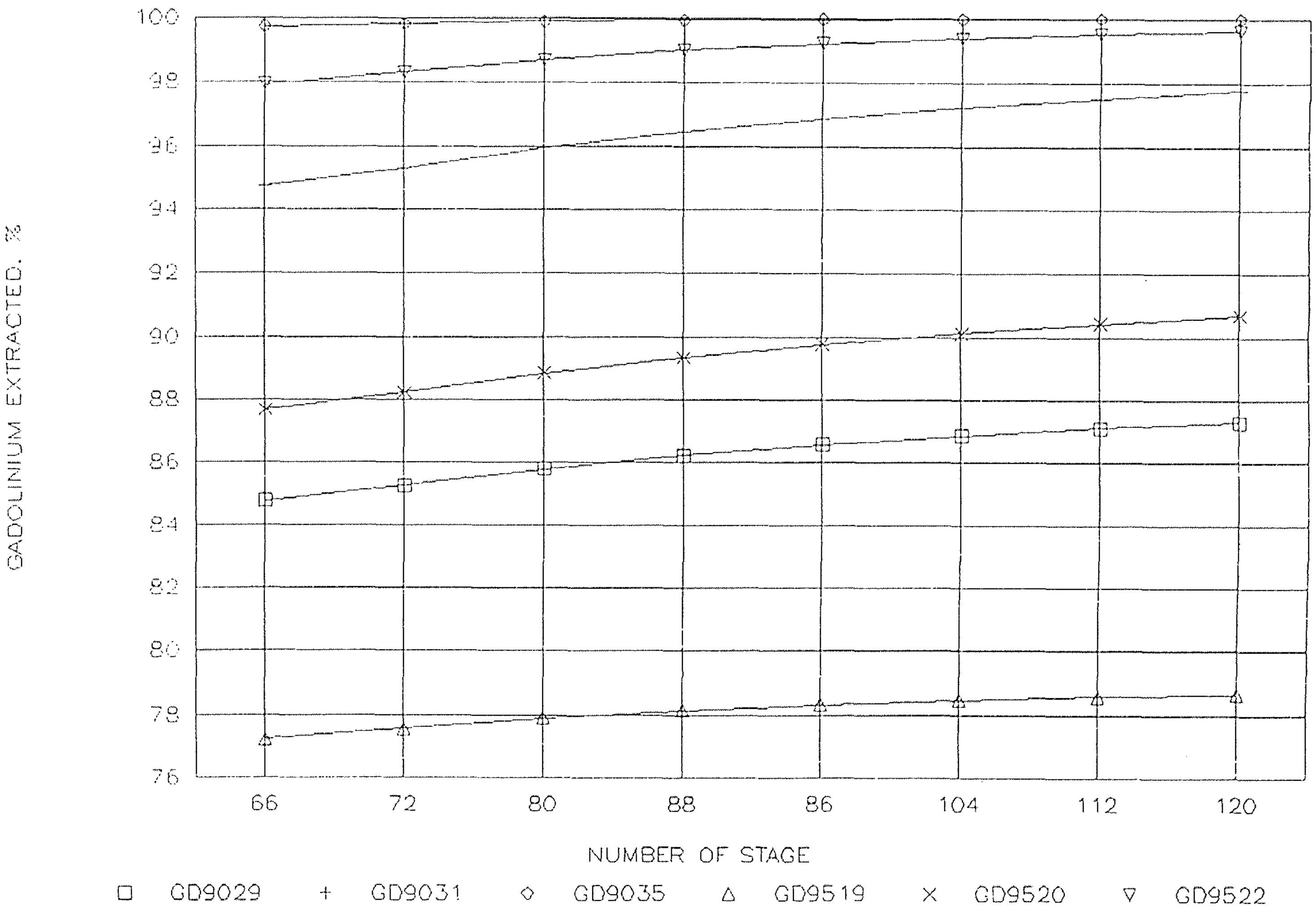

Figure 6.3 The Effect of Number of Stages on the Separation of Gd from the Sub-group Gd-La, Gd Extracted %.

The first two characters in the test code GD9519 tells which rare earth was tested, the next two digits represents the HNO_3 acid strength in the extraction system, and the last two digits means extractant flow rate in l/h. In the GD9519 case, gadolinium was tested in the 9.5 N HNO_3 acid strength aqueous solution with 1.9 l/h of extractant flow. The guideline for constructing test codes
will be used throughout this research.

6.5 The Purification of Europium

Europium is an expensive and important raw material for the high technology area. Many high technology industries demand very high purity europium. Europium is being used as the additives material for colored cathode ray tubes. Obviously, it becomes more and more important for many rare earths producers to manufacture ultrahigh purity europium by more efficient methods. The retail price for 5 g of 99.9 % europium oxide is $46.50 in 1992, it costs $63.45 for 5 g of 99.99% europium oxide, however, when the purity increases to 99.999 %, the price goes up to $96.65 for 5 g of europium oxide (70). Because so many factors dominate the europium purification process, we decided to institute a systematic investigation, with the objective of obtaining key process parameters.

We discussed the separation of gadolinium from the sub-group Gd-La in Section 6.4. Since the extractability of gadolinium is the highest among all species in the sub-group Gd-La, gadolinium was extracted by TBP and others remained intact in the raffinate stream. After adjustment of rare earths concentration and acidity of raffinate, the unextracted lighter-weighted rare earth sub-group Eu-La was sent to the extraction circuit for europium separation and purification as feed. The composition (wt %) of feed stream is:

Component	**Wt %**	**Component**	**Wt %**
Eu_2O_3	0.6630	Sm_2O_3	5.4184
Nd_2O_3	34.9187	Pr_2O_3	10.2349
Ce_2O_3	3.0102	La_2O_3	45.7555

Because the europium oxide is the most extractable specie among all contents in the feed stream, the separation process is accomplished by extracting europium nitrate into the organic phase. The europium in the organic phase is then continue processed with more stages in the extraction system until 99.9% or higher purity was reached.

Since the commercial rare earth separation technologies are proprietary, specific operation details can not be easily found. Enormous efforts were necessary in finding acceptable process conditions. A 100% stage efficiency was used in all of the cases studied. The operating conditions we used in purifying europium oxide are:

Number of Stages: 42 to 132 stages.

Feed: 9.8-10.2 N HNO_3, 1.0 l/h, with rare earths 100.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.8-10.2 N HNO_3, 1.9-2.6 l/h.

Scrub Solution: 9.8-10.2 N HNO_3, 2.0 l/h.

Tables 6.4 to 6.19 give the recoveries and purities of the europium product with different stage numbers and operating conditions. The effect of the number of stages on europium recoveries and purities are shown in Figures 6.4 to 6.13. Table 6.20 and Figure 6.14 show the stage numbers effect on europium product impurities, mainly, samarium in europium product. Tables 6.4, 6.20 and Figures 6.4, 6.9, 6.14 are located in the following pages, all other tables and figures can be found in the Appendices A and B, respectively.

6.6 Discussions

Because the stability limitation of ISR algorithm was reached, cases with 10.3 N or higher acidity of HNO_3 were not obtained.

Figures 6.4 to 6.13 explicitly show, that the europium recovery and product purity are functions of aqueous acidity, feed to extractant flow ratio, aqueous to organic

Table 6.4 The Effect of Number of Stages on Europium Purification, HNO_3 9.8 N, TBP 2.4 l/h.

STAGE	% RECOVERY	% PURITY
42	72.2573	97.9969
48	73.0191	99.0389
54	73.5814	99.5394
60	74.0000	99.7796
66	74.3139	99.8945
72	74.5507	99.9494
78	74.7303	99.9758
84	74.8670	99.9884
90	74.9713	99.9944
96	75.0512	99.9973
102	75.1124	99.9987
108	75.1594	99.9994
114	75.1955	99.9997
120	75.2233	99.9999
126	75.2446	99.9999
132	75.2610	99.9999

Feed 9.8 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.4 l/h, equilibrated with 9.8 N HNO_3
Scrub 9.8 N HNO_3, 2.0 l/h

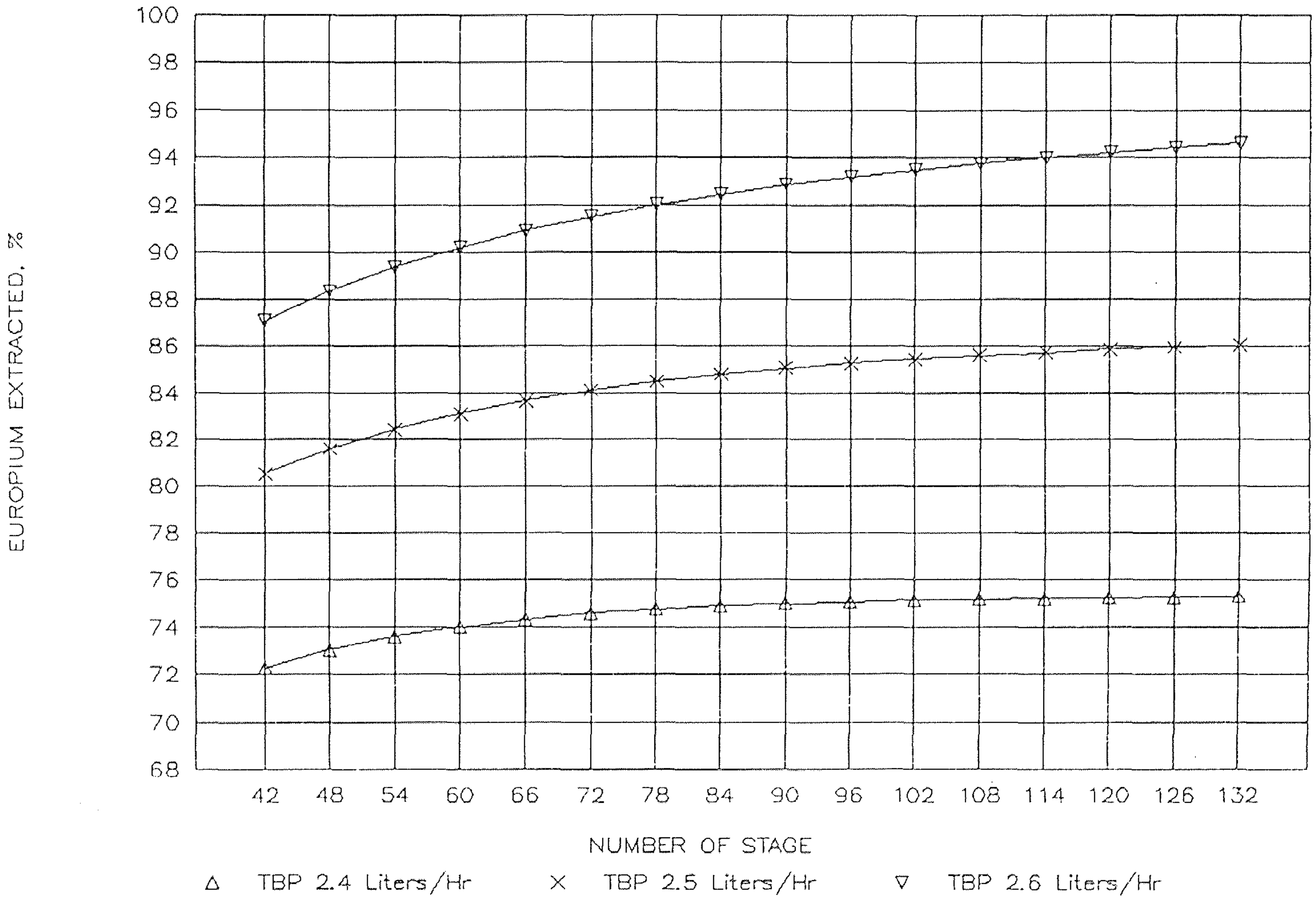

Figure 6.4 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO_3 9.8 N.

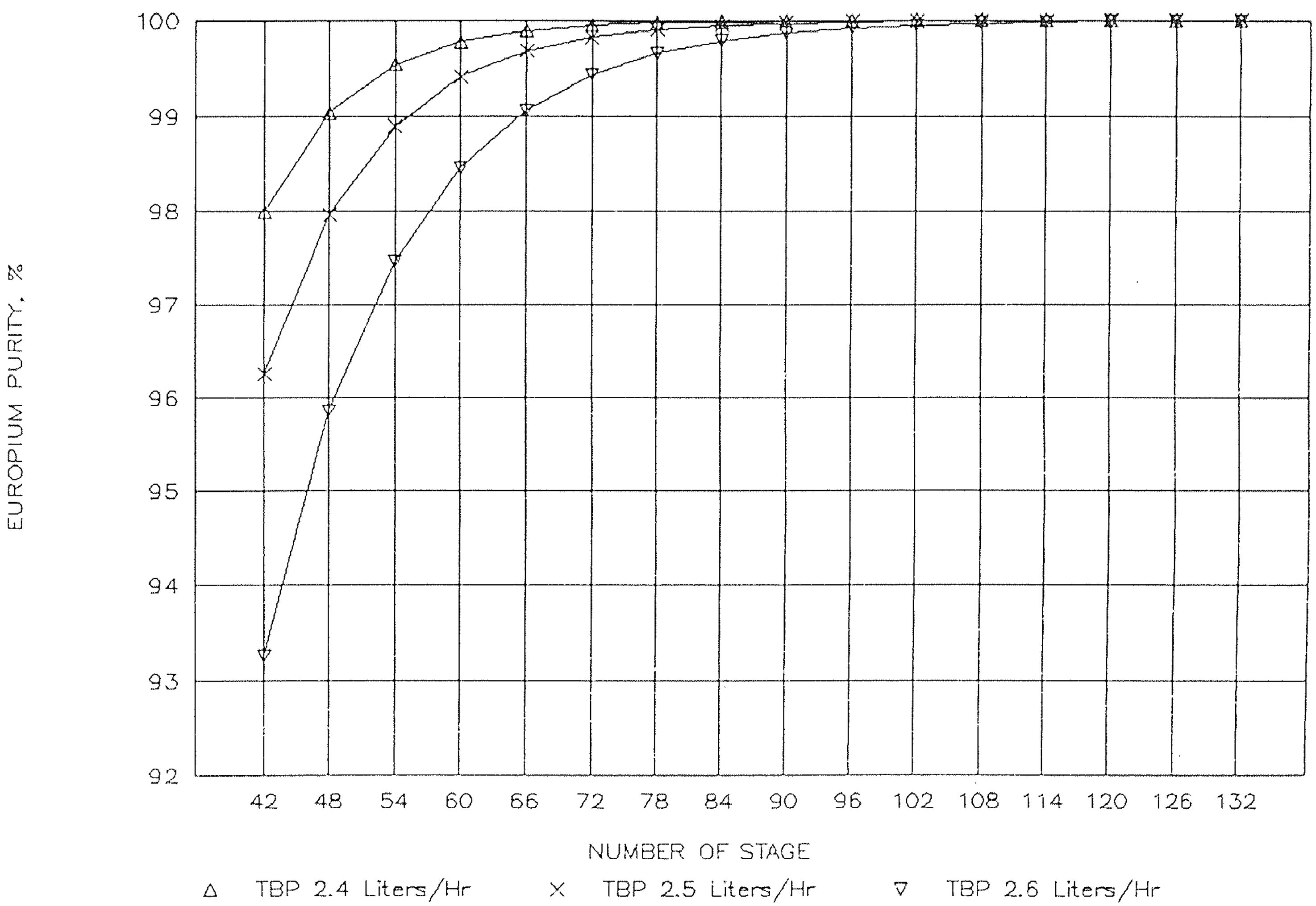

Figure 6.9 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 9.8 N.

Table 6.20 The Effect of Number of Stages on Europium Product Impurities, Samarium in Product %.

	CASE NUMBERS		
STAGE	EU10219	EU10220	EU10221
42	1.6762	3.8164	8.1025
48	0.7907	2.1104	5.2355
54	0.3726	1.1633	3.3678
60	0.1756	0.6404	2.1603
66	0.0829	0.3525	1.3834
72	0.0391	0.1940	0.8850
78	0.0185	0.1068	0.5659
84	0.0087	0.0588	0.3618
90	0.0041	0.0322	0.2313
96	0.0020	0.0179	0.1478
102	0.0009	0.0099	0.0945
108	0.0004	0.0054	0.0604
114	0.0002	0.0030	0.0386
120	0.0001	0.0017	0.0247
126	0.0001	0.0009	0.0158
132	0.0001	0.0005	0.0101

Feed 10.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 1.9-2.1 l/h, equilibrated with 10.2 N HNO_3
Scrub 10.2 N HNO_3, 2.0 l/h

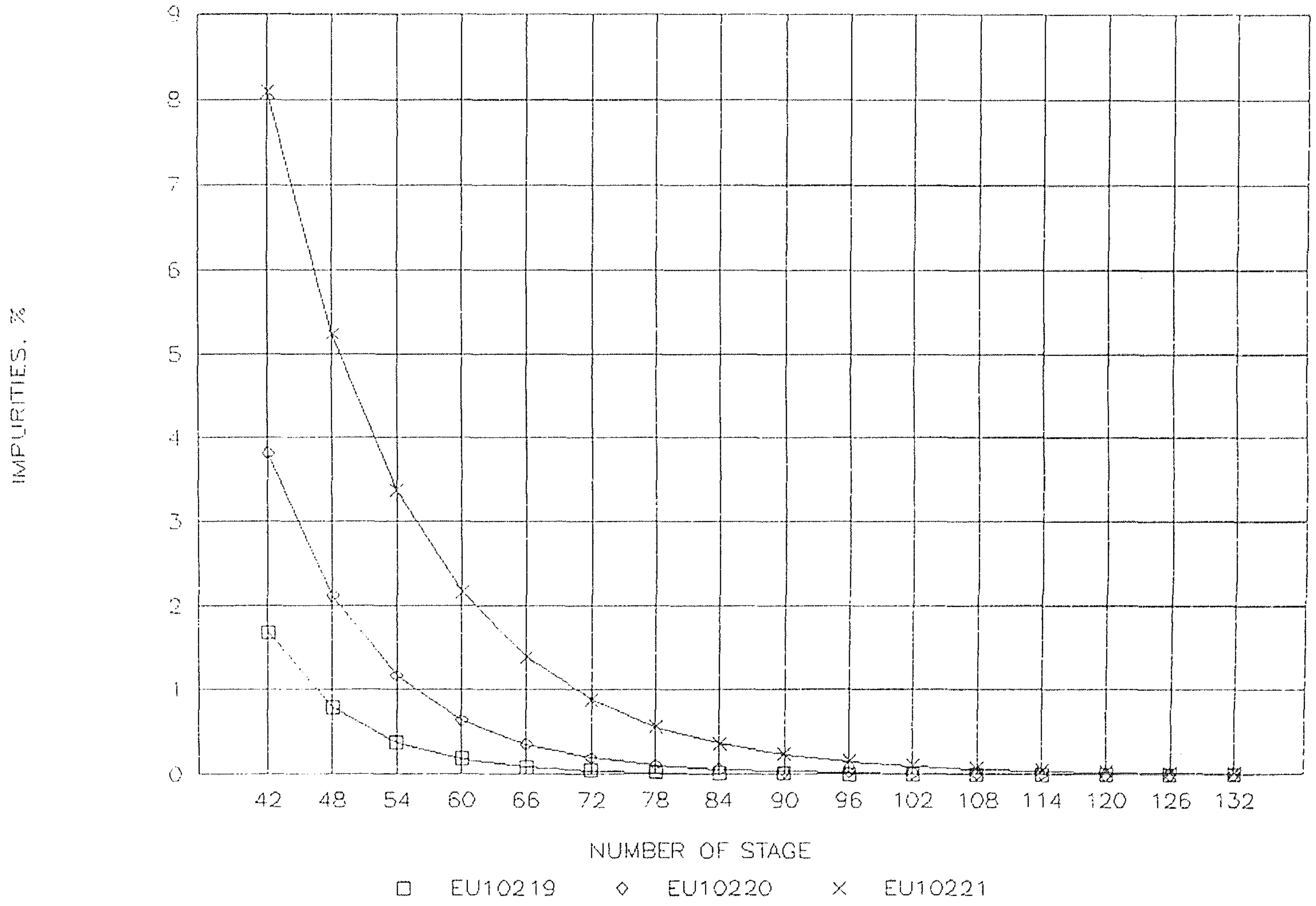

Figure 6.14 The Effect of Number of Stages on Europium Product Impurities, Samarium in Product %.

flow ratio, and the number of stages. Figures 6.4 to 6.13 also show that the europium extraction increases as the number of stages increases, but the rate of change gradually tapers off with large stage numbers, if the other operating conditions remain the same. If a larger ratio of solvent to the feed was used, the europium extraction rate increases, however, the product purity decreases. If the ratio of solvent to feed decreased, the europium purity decreased and the product recovery increases. Clearly, a balance lies between the recovery rate and product purity.

This observation leads to the conclusion that a cost analysis and optimization is necessary procedure to arrive at the rare earth separation and purification process design.

CHAPTER 7

PURIFICATION OF YTTRIUM

7.1 The Purification Of Yttrium

Yttrium is a very valuable commodity, it is also a very importment material in certain industries, especially in the electronic industry. For example, high purity (99.9% or higher) of yttrium is one of the key raw materials for making color televisions and personal computer color monitors.

As discussed earlier, the rare earth nitrate extraction into TBP organic phase increases in the order of increasing atomic number. Because of their similar structures and chemical properties, the separation of rare earths into individual components is rather difficult, especially beyond Tb in the atomic number raw. Therefore, high purity yttrium is very expensive. The retail price for 50 g of 99.99 % yttrium oxide is $25.0 in 1992, however, when purity increases to 99.999 %, the price goes up more than three-fold to $84.55 (70). Because so many variables are involved in purification process, a systematic approach seems necessary. The ultimate goal is to gain crucial process information.

The aim of yttrium purification is to improve the yttrium purity to 99.9% or higher. It is assumed that the sub-group of Lu_2O_3, Y_2O_3 and Yb_2O_3 have been separated from the bulk of rare earth oxides in the Jiangxi mineral sample by the manner of solvent extraction. The species Lu_2O_3, Y_2O_3 and Yb_2O_3 were extracted into the TBP organic phase from the aqueous phase. After stripping with low acidity nitric acid solution (1 - 2 N), the components Lu_2O_3, Y_2O_3 and Yb_2O_3 in the organic phase were concentrated in the aqueous phase.

The species Lu_2O_3 and Yb_2O_3 have higher distribution coefficients than that of Y_2O_3 in the HNO_3-H_2O-TBP system for an acidity range of 6 to 15 N. Thus, we took advantage of the lower yttrium oxide distribution coefficients and larger separation factor of Yb/Y, to separate Y_2O_3 from the mixture of Lu_2O_3, Yb_2O_3 and Y_2O_3 by extracting Lu_2O_3 and Yb_2O_3 into the organic phase, and leave Y_2O_3 in the aqueous solution.

The Lu_2O_3, Yb_2O_3 and Y_2O_3 mixture composition (wt %) after stripping and distribution coefficient at acidity 9.0 N in the aqueous phase are tabulated below:

Component	Wt %	K_d
Lu_2O_3	0.9288	8.84
Yb_2O_3	6.1919	6.58
Y_2O_3	92.8793	3.68

Since commercial rare earth processes are highly proprietary, specific details are not readily available. Therefore, tremendous efforts were made in searching the appropriate process conditions. The multicomponent, multistage, counter-current liquid-liquid extraction computer program was used to simulate the extraction processes. Again, the stage efficiency was assumed to be 100%. After hundreds of cases were simulated and studied, the key process parameters such as: acidity in the aqueous phase, the rate ratio of the organic phase to feed, and rate ratio of the organic phase to the aqueous phase were found. We believe these process conditions are acceptable to the rare earths industries. The critical parameters are summarized below:

Number of Stages: 18 to 144 stages.

Feed: 6.1-6.4 N HNO_3, 1.0 l/h, with rare earths 10.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 6.1-6.4 N HNO_3, 2.5-3.4 l/h.

Scrub Solution: 6.1-6.4 N HNO_3, 2.0 l/h.

The recoveries and purities of yttrium product with different operating conditions were tabulated in Tables 7.1 to 7.20. The graphical representation of the effect of the number of stages on yttrium recovery and purity was made by plotting the recovery and purity data at the same aqueous acidity with different organic flow rates, and is shown in Figures 7.1 to 7.4 for yttrium recovery, and in Figures 7.5 to 7.8 for yttrium purity, respectively. Table 7.22 and

Figure 7.9 show the effect of stage numbers on yttrium product impurities, or more specifically, the lutetium and ytterbium in europium product. Tables 7.1 and 7.22, and Figures 7.1, 7.5 and 7.9 were placed in the following pages as representative of all cases that have been studied. The remaining tables and figures can be seen in Appendices A and B, respectively.

7.2 Discussions

Figures 7.1 and 7.5 have shown, that the yttrium recovery and product purity increases as the number of stages increases, but a gradual increase is obtained with large stage numbers. An effective way to increase recovery rate is by extracting the Lu_2O_3 and Yb_2O_3 by lowering the ratio of solvent to feed. However, at lower organic flow rate, the yttrium product purity decreases at lower stage numbers. On the contrary, if the ratio of solvent to feed increases, the yttrium purity increases accordingly, but low recovery will be achieved. Obviously, there is a balance between the recovery rate and product purity.

This observation enable us to draw the same conclusion as we did in the previous chapter and leads to the subject of the next chapter: the optimal design of europium and yttrium separation and purification systems. Factors involved in the optimization process are feed concentration, stage numbers, recovery rate, product purity, capitol costs, operating costs, interest rate, product sale price, etc.

Table 7.1 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.1 N, TBP 3.0 l/h.

STAGE	% RECOVERY	% PURITY
18	94.2405	98.3780
24	96.8635	98.7073
30	98.2502	98.9244
36	99.0124	99.0770
42	99.4398	99.1899
48	99.6815	99.2770
54	99.8188	99.3464
60	99.8969	99.4031
66	99.9414	99.4504
72	99.9666	99.4905
78	99.9810	99.5250
84	99.9892	99.5549
90	99.9939	99.5812
96	99.9965	99.6044
102	99.9980	99.6251
108	99.9989	99.6437
114	99.9994	99.6604
120	99.9996	99.6756
126	99.9998	99.6894
132	99.9999	99.7020
138	99.9999	99.7136
144	100.0000	99.7243

Feed 6.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.0 l/h, equilibrated with 6.1 N HNO
Scrub 6.1 N HNO_3, 2.0 l/h

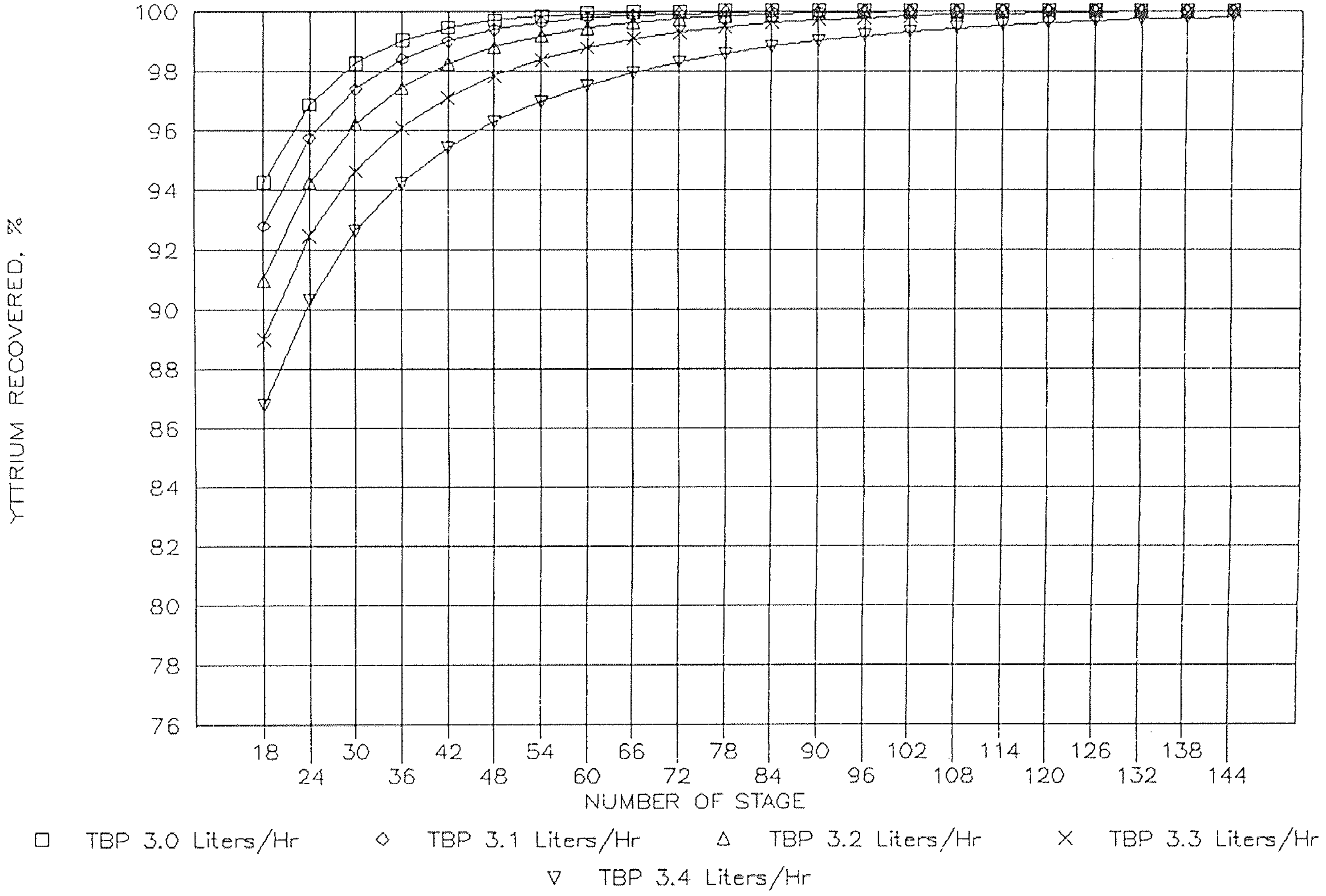

Figure 7.1 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO_3 6.1 N.

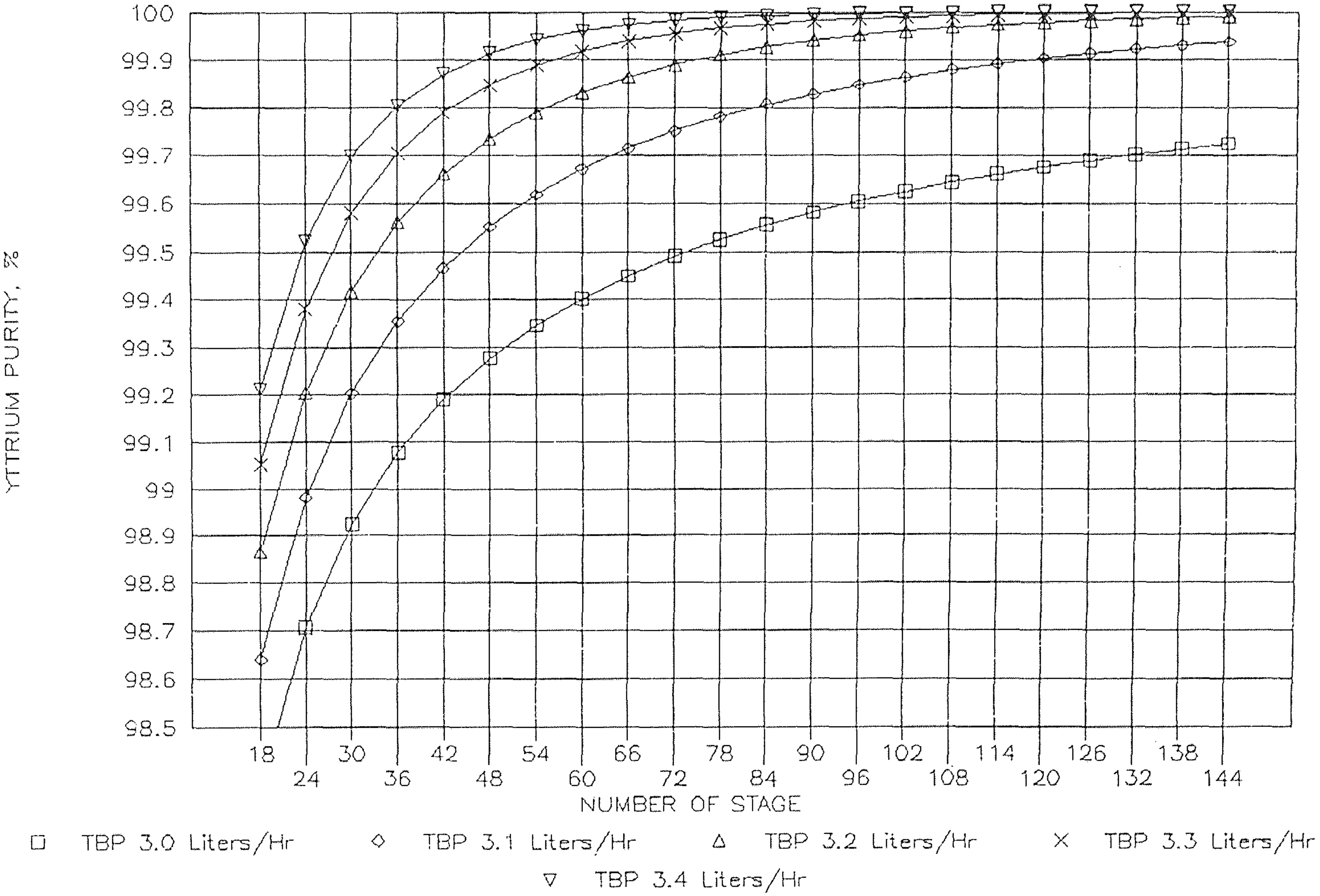

Figure 7.5 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO_3 6.1 N.

Table 7.22 The Effect of Number of Stages on Yttrium Product Impurities, Lu and Yb in Product %.

	CASE NUMBERS					
STAGE	Y6425	Y6426	Y6427	Y6428	Y6429	Y6430
18	1.3693	1.0962	0.8757	0.7002	0.5620	0.4537
24	1.0256	0.7552	0.5522	0.4032	0.2955	0.2182
30	0.8035	0.5439	0.3630	0.2241	0.1607	0.1080
36	0.6499	0.4038	0.2451	0.1475	0.0891	0.0544
42	0.5378	0.3060	0.1685	0.0916	0.0500	0.0277
48	0.4526	0.2355	0.1172	0.0573	0.0282	0.0142
54	0.3857	0.1831	0.0821	0.0361	0.0160	0.0073
60	0.3321	0.1436	0.0579	0.0228	0.0091	0.0037
66	0.2881	0.1132	0.0410	0.0145	0.0052	0.0019
72	0.2516	0.0897	0.0291	0.0092	0.0030	0.0010
78	0.2221	0.0714	0.0207	0.0058	0.0017	0.0005
84	0.1948	0.0569	0.0148	0.0037	0.0010	0.0003
90	0.1724	0.0455	0.0105	0.0024	0.0006	0.0002
96	0.1531	0.0365	0.0075	0.0015	0.0003	0.0001
102	0.1363	0.0292	0.0054	0.0010	0.0002	0.0001
108	0.1217	0.0235	0.0038	0.0006	0.0001	0.0001
114	0.1088	0.0189	0.0027	0.0004	0.0001	0.0001
120	0.0975	0.0152	0.0020	0.0003	0.0001	0.0001
126	0.0875	0.0122	0.0014	0.0002	0.0001	0.0001
132	0.0787	0.0098	0.0010	0.0001	0.0001	0.0001
138	0.0708	0.0079	0.0007	0.0001	0.0001	0.0001
144	0.0638	0.0064	0.0005	0.0001	0.0001	0.0000

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.5-3.0 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

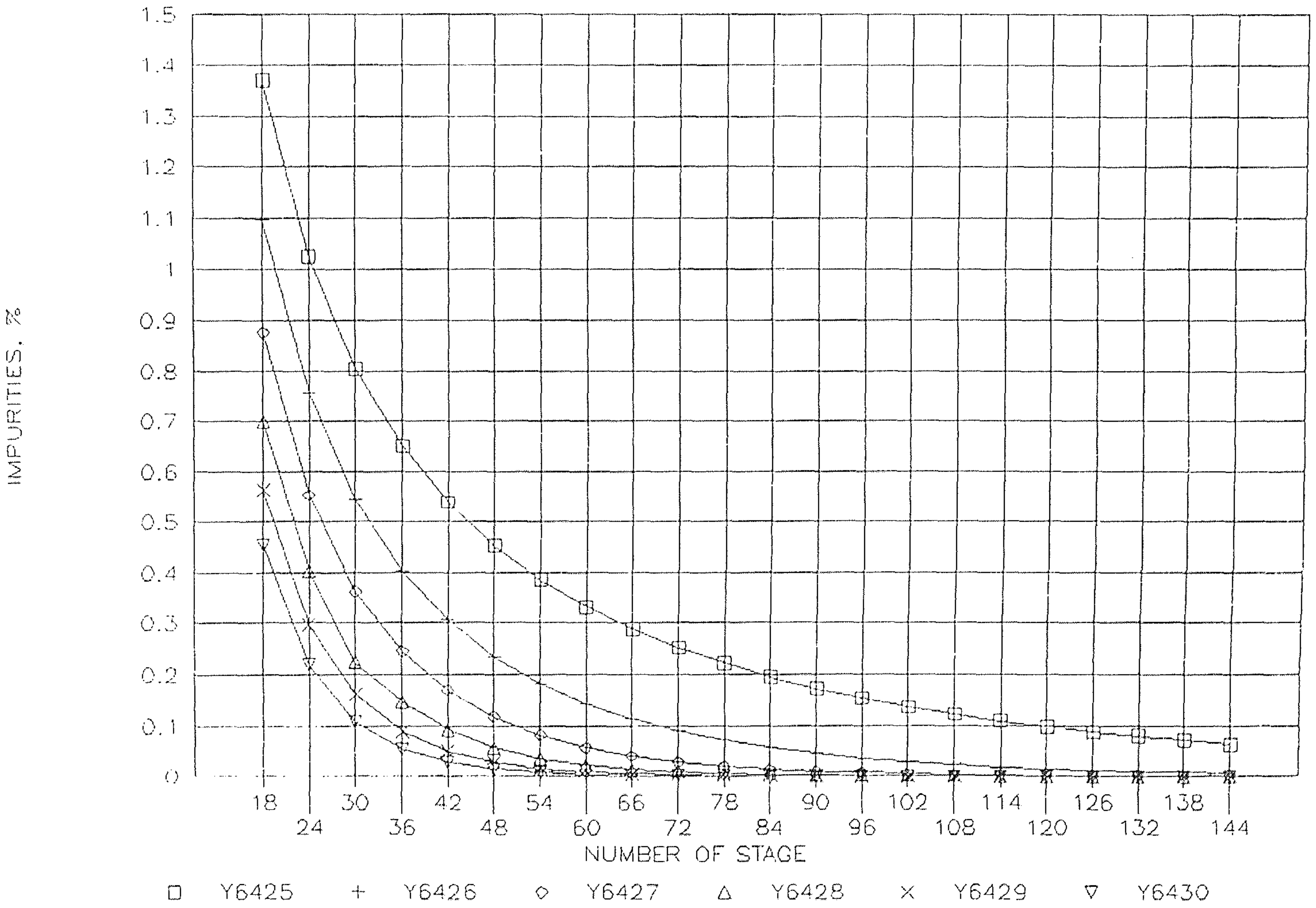

Figure 7.9 The Effect of Number of Stages on Yttrium Product Impurities, Lu and Yb in Product %.

CHAPTER 8

ECONOMIC ANALYSIS

8.1 General Principles

The economic analysis and optimization of processes involving solvent extraction are particularly important. The values of the solutes considered for recovery must be compared against the cost of extraction. Chemical processing industries generally consume large quantities of raw materials, as well as energy and capital. As mentioned earlier, the liquid-liquid extraction process is employed for separation when it is the only method available or the most economical technique when compared with alternative separation processes. Extraction processes may not be selected unless they have shown clear economic advantages.

Generally, economic analysis consists of the analysis of capital investment and operating costs (69).

8.2 Capital Investment

The capital investment is the amount of money spent to build the extraction plant. Before a chemical plant can be put into operation, a large sum of money must be supplied to purchase and install the necessary machinery and equipment. Land and service facilities must be obtained, and the plant must be erected complete with all piping, controls, and services. Besides, the money needed for the expenses of plant operation must also be available.

For a rare earths extraction system, the following factors may dominate the capital investment:

1. Number of stages, the number of mixer-settlers.
2. The size of the mixing and settling devices.
3. Flow rate and flow ratios.
4. Pumps, piping and instrumentation.
5. Land, site preparation, site preparation.
6. Utilities and buildings.
7. Raw materials and supplies carried in stocks.

There are many ways of estimating the total capital investment. Peters and Timmerhaus (71) proposed a method for estimating capital investment, their technique directly relates the total capital cost to the expenses for purchased equipment by a multiplying factor.

8.3 Operating Costs

Capital investment is the expense of obtaining a working plant, while the operating costs are the charges involved in running the plant after it has been constructed. Generally, the cost of an extraction operation is incurred for the following items:

1. Costs for feed, solvent and nitric acid.
2. Cost of preconditioning the feed stream. The feed may require acidity adjustment, or removal of unwanted materials.
3. Cost of pre-equilibration of the solvent may be required. For example, the solvent TBP is pre-equilibrated

with nitric acid in the cases of europium and yttrium separation and purification.

4. Cost of scrubbing and stripping. These are necessary operations for the rare earths extraction system. These steps involve extra operating costs for chemical agents, labor, power and maintenance.

5. Cost of solvent losses. The charges for replacing lost solvent are part of the regular operation cost. The factors which cause the solvent losses are: solubility of extractant in the raffinate solution; entrainment of extractant in the raffinate phase; degradation of extractant; crud formation; evaporation of extractant and physical losses due to leaks or spillages.

6. Labor and maintenance costs. The cost of operators together with the supervisors, usually account for a part of the operation costs.

7. Energy costs. Power will be required for mixers, instruments, pumps, lighting and heating of the plant.

8. Unrecovered desirable solute in the raffinate phase can also account for an increase in operating costs.

8.4 Total Production Cost Function

Based on the discussions of capital investments in section 8.2 and operating costs in section 8.3, the total production cost function for liquid-liquid extraction operations is then given by:

$$\text{Total Production Cost} = \text{Capitol Investment} + \text{Operating Costs} \quad (8.1)$$

8.5 Case Study 1: The Separation And Purification Of Europium

It was decided that europium is to be separated from 54.5 kg/hr of the sub-group Eu-La of rare earth oxides raw material from Jiangxi Province, China and further be purified to 99.9% or higher purity in the HNO_3-H_2O-TBP system by the solvent extraction process.

Two processes are involved in above operation: separating the europium from the sub-group Eu-La of Jiangxi mineral raw material; and then purifying the separated europium to the desired purity. The operating conditions for separation and purification of europium were discussed in Section 6.5.

The process parameters for the europium separation and purification are listed below:

Number of Stages: 42 to 132 stages.

Feed: 9.8-10.2 N HNO_3, 545 l/h, with rare earths 100.0 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.8-10.2 N HNO_3, 1035-1420 l/h.

Scrub Solution: 9.8-10.2 N HNO_3, 1090 l/h.

McCabe and Smith (74) suggested that 5 minutes resident time for mixing and 25 minutes for settling are typical. Their suggestion was used as minimum resident time criterion for mixer-settler extractor design. Denver Mineral Engineers, Inc. (73) recommended turbine pumping-mixing type mixer-settler be used, because this design allows entire system to be mounted on a single level without the need for interstage pumps. Turbine position may be varied to optimize pumping and mixing performance. Their design consists of 100 gallon mix tanks and 450 gallon settler tanks, and with 1/2 HP pump mix turbine impeller mixers. The budgetary prices for 80 stages system is $650,000.00, and for 150 stages system is $1,210,000.00.

The mixer-settlers system suggested by Denver Mineral Engineers, Inc. (73) was used for cost analysis. The total capital investment for this operation per stage of mixer-settler was estimated by the technique proposed by Peters and Timmerhaus (71). Their method is to relate the total capital cost to the expenses for purchased equipment by a multiplying factor. In the following page, Table 8.1 exhibits the estimated total capital investment per stage of mixer-settler.

Other important cost parameters are: the extraction units are operated 8 hours per shift, 3 shifts per day and 350 days per year. For a 40 stage system, one operator, one half maintenance man and one half supervisor (share with other process unit) are required per shift. Increment of one

Table 8.1 The Estimated Total Capital Investment per Stage of Mixer Settler.

	Direct costs
Cost for mixer-settler per stage	$8,100
Purchased equipment-installation	$3,807
Instrumentation and controls	$1,458
Piping (installed)	$5,346
Electrical (installed)	$891
Buildings (including services)	$1,458
Yard improvements	$810
Service facilities (installed)	$4,050
Land	$486
Total direct plant cost	$26,406
	Indirect costs
Engineering and supervision	$2,673
Construction expenses	$3,321
Total direct and indirect plant costs	$32,400
Contractor's fee	$1,620
Contingency	$3,240
Fixed-capital investment	$37,260
Working Capital	$5,589
Total Capital investment	$42,849

1. Cost for mixer-settler was estimated by Denver Mineral Engineers, inc. (73).
2. Turbine-Pump type of mixer-settler was proposed (73), including 100 gallon mixing tank, 450 gallon settler tank, and 1/2 HP mix turbine impeller mixer.
3. All cost factors are based on Peters and Timmerhaus (71).

operator for every 40 mixer-settlers increases. The annual cost for each labor is $40,000.00. The cost for replacing the lost solvent is assumed to be $10.00 per stage per day.

The 10 year straight line method was used in calculating the equipment and facilities depreciation. The capital investment of this extraction process plant is also compounded by an annual 8% interest rate.

Based on the retail prices suggested by Aldrich Catalog (70), allowing overhead expenses, discount for large quantities, federal and local taxes, and profits, the whole sale prices for europium oxide with different grades were assumed: $1860.00/kg for 99.9% purity grade, $2,538.00/kg for 99.99% purity grade, and $3,866.00/kg for 99.999% purity grade.

The total production cost for the separation and purification of europium, which is based on the assumptions we made in this section and on the equation (8.1) is readily obtained. The results are expressed as dollars/kg of europium oxide produced.

$$\textbf{Total production cost} = \textbf{Capitol cost} + \textbf{Cost of Labor} + \textbf{Cost of solvent loss} + \textbf{Loss from unrecovered desirable solute} + \textbf{Cost of interest} \qquad (8.2)$$

A few items which were discussed in Sections 8.2 and 8.3 are not included in equation (8.1), because neither they are influential nor easily estimate.

Table 8.2 shows the total production costs for all europium purification cases we have investigated. Each case which is shown in Table 8.2 also consists of three sub-cases, because final europium oxide product has three grades of purity. The parameters for the least purification costs are: 99.9% europium, case EU10221, 102 stages; 99.99% europium, case EU10220, 102 stages and 99.999% europium, case EU10220, 126 stages. As we have mentioned in Chapter 6, cases with 10.3 N HNO_3 are not available, due to the stability limitation of ISR algorithm was reached. Table 8.3 tabulates the break down for the minimum production costs in all three sub-cases with different purity grades.

8.6 Case Study 2: The Purification Of Yttrium

Similar to the cost analysis for the separation and purification of europium oxide in Case Study 1, this section deals with the purification of yttrium oxide from the mixtures of lutetium, ytterbium and yttrium. The objective is to improve the yttrium purity to 99.9% of higher. Details of purification processes were discussed in Chapter 7.

The process parameters for this operation are:

Number of Stages: 18 to 144 stages.

Feed: 6.1-6.4 N HNO_3, 500 l/h, with rare earths
10.0 g/l of feed solution.

Table 8.2 Costs for Europium Oxide Purification.

	Eu Purity		
Cases	99.9%	99.99%	99.999%
EU9824	$1,156.88	$1,509.39	$2,027.69
EU9825	$828.56	$1,065.17	$1,411.72
EU9826	$692.78	$860.32	
EU9922	$1,275.11	$1,678.39	$2,261.55
EU9923	$884.37	$1,147.74	$1,477.84
EU9924	$707.73	$825.22	
EU9925	$616.86		
EU10021	$1,012.53	$1,311.44	$1,741.02
EU10022	$707.59	$893.06	$1,130.86
EU10023	$607.15	$749.96	
EU10120	$968.14	$1,248.97	$1,646.85
EU10121	$667.44	$836.63	$1,045.71
EU10122	$584.46	$724.16	
EU10219	$806.19	$1,020.66	$1,301.06
EU10220	$619.40	$697.11	$853.20
EU10221	$564.03		

1. Costs are in dollars/kg of Europium Oxide.
2. Costs data are based on 3.0 metric tons per year.

Table 8.3 Cost Analysis for the Separation and Purification of Europium Oxide.

Eu Purity	99.9%	99.99%	99.999%
Equipment	$147.06	$153.04	$187.20
Capital Cost	$147.06	$153.04	$187.20
Labor	$161.52	$168.12	$208.04
Solvent Loss	$120.13	$125.04	$152.91
Unrecov. Eu	$17.66	$128.48	$155.30
Interest	$117.66	$122.43	$149.75
Operating Cost	$416.97	$544.07	$666.00
Total Cost	$564.03	$697.11	$853.20

1. Design base: 3.0 metric tons of europium oxide per year.
2. Costs in Dollar/Kg of Europium Oxide.
3. 10 year straight line depreciation method used.
4. 8.0% interest rate.
5. Operator costs $40,000 per year.
6. Mixer-settlers required for
   Eu 99.9%: 102
   Eu 99.99%: 102
   Eu 99.999%: 126

Extractant: TBP pre-equilibrated with 6.1-6.4 N HNO_3, 1250-1700 l/h.

Scrub Solution: 6.1-6.4 N HNO_3, 1000 l/h.

The mixer-settler system proposed by Denver Mineral Engineers, Inc (73) is still within the design criterion, and can be used for this operation. All other cost parameters remain the same as compared to Case Study 1. Based on the same rule we have used for the whole sale prices of europium oxide, the following yttrium oxide whole sale prices was thus assumed: for 99.9% purity product, the price is $65.00/kg, for 99.99% purity product, the price is $83.00/kg, and for 99.999% purity product, the price is $282.00/kg.

The total production cost function which was described by equation (8.2) is also valid for yttrium purification.

Table 8.4 shows the total production costs for all yttrium oxide purification cases we have studied. Similar to europium purification in Case Study 1, each case shown in Table 8.4 consists of three sub-cases, because yttrium oxide product purity has three grades: 99.9%, 99.99% and 99.999%. The process parameters for the minimum costs for yttrium purification are: yttrium 99.9%, case Y6134, 48 stages, yttrium 99.99%, case Y6428, 72 stages and yttrium 99.999%, case Y6428, 102 stages. The break down for the minimum production costs in all three purity grades are shown in Table 8.5.

Table 8.4 Costs for Yttrium Oxide Purification.

	Y Purity		
Cases	99.9%	99.99%	99.999%
Y6131	$45.33		
Y6132	$29.58	$52.73	
Y6133	$25.72	$40.43	
Y6134	$24.74	$35.28	$47.68
Y6230	$35.30	$58.45	
Y6231	$31.57	$44.63	
Y6232	$30.95	$41.29	$49.58
Y6233	$32.87	$37.57	$53.07
Y6234	$32.89	$41.19	$65.28
Y6328	$37.15	$65.14	
Y6329	$33.92	$50.46	$68.31
Y6330	$32.73	$43.21	$61.21
Y6331	$31.78	$43.78	$68.99
Y6332	$36.52	$48.36	$82.11
Y6425	$46.33		
Y6426	$28.13	$49.54	
Y6427	$25.05	$37.62	$49.92
Y6428	$25.54	$31.37	$44.45
Y6429	$25.49	$33.67	$55.15
Y6430	$30.29	$39.25	$70.95

1. Costs are in dollars/kg of Yttrium Oxide.
2. Costs data are based on 4.2 metric tons per year.

Table 8.5 Cost Analysis for the Purification of Yttrium Oxide.

Y Purity	99.9%	99.99%	99.999%
Equipment	$5.09	$7.58	$10.59
Capital Cost	$5.09	$7.58	$10.59
Labor	$8.90	$8.85	$11.63
Solvent Loss	$4.16	$6.19	$8.65
Unrecov. Y	$2.52	$2.68	$5.09
Interest	$4.07	$6.07	$8.49
Operating Cost	$19.65	$23.79	$33.86
Total Cost	$24.74	$31.37	$44.45

1. Design base: 4.2 metric tons of yttrium oxide per year
2. Costs in Dollar/Kg of Yttrium Oxide.
3. 10 year straight line depreciation method used.
4. 8.0% interest rate.
5. Operator costs $40,000 per year.
6. Solvent loss $10.0 per stage per day.
7. Mixer-settlers required for
   - Y 99.9%: 48
   - Y 99.99%: 72
   - Y 99.999%: 102

8.7 Case Study 3: Separation Of Gadolinium From The Sub-Group Gd-La Of Jiangxi Mineral Sample

The separation of gadolinium from the sub-group Gd-La of Jiangxi mineral sample is a important operation too. Separation and purification of europium operation can not be proceed unless the gadolinium has been separated earlier. Separation of gadolinium was discussed in Section 6.4.

Due to the small separation factor of Gd/Eu, the separation of gadolinium from the sub-group Gd-La is rather difficulty. During separation process, gadolinium accompanied by some europium were extracted into the organic phase from the aqueous phase. Even with large stage numbers, clean-cut separations were still not easily obtained.

The optimum process parameters for this operation are:

Number of Stages: 66 to 120 stages.

Feed: 9.5 N HNO_3, 440.0 l/h, with rare earths 133 g/l of feed solution.

Extractant: TBP pre-equilibrated with 9.5 N HNO_3, 880.0 l/h.

Scrub Solution : 9.5 N HNO_3, 836.0 l/h.

The mixer-settler system suggested by Denver Mineral Engineers, Inc (73) is still available for this operation. All other cost parameters remain the same as Case Study 1. The whole sale prices for gadolinium oxide were estimated based on the same rule we used before. The whole sale prices used in cost analysis are: \$250.00/kg for 99.9% purity gadolinium, \$1,444.00/kg for 99.99% purity gadolinium. The total production cost function which was described by equation (8.2) is also valid for gadolinium.

Only case GD9519 has successfully produced 99.99% purity gadolinium. Figure 8.1 shows the total production costs for case GD9519. The minimum point occurs between stages 80 to 88. Figure 8.1 also shows a step jump in the production cost at stage 120, this is attributed to the increase of one more operator per shift in operation.

8.8 Discussions

The feed concentration also plays a role in the process economics. Ritcey (72) reported the relationship between feed concentration and the processing costs for systems covering the acidic and basic extraction. Due to insufficient of experimental equilibrium data for higher concentration of rare earths in the feed, investigation was not conducted.

The optimum number of mixer-settlers for europium oxide separation and purification operation are 102 for 99.9% or 99.99% europium, and 126 for 99.999% europium product. The optimum process design for yttrium oxide purification includes an extraction system with 48 mixer-settlers for 99.9% purity yttrium, 72 mixer-settlers for

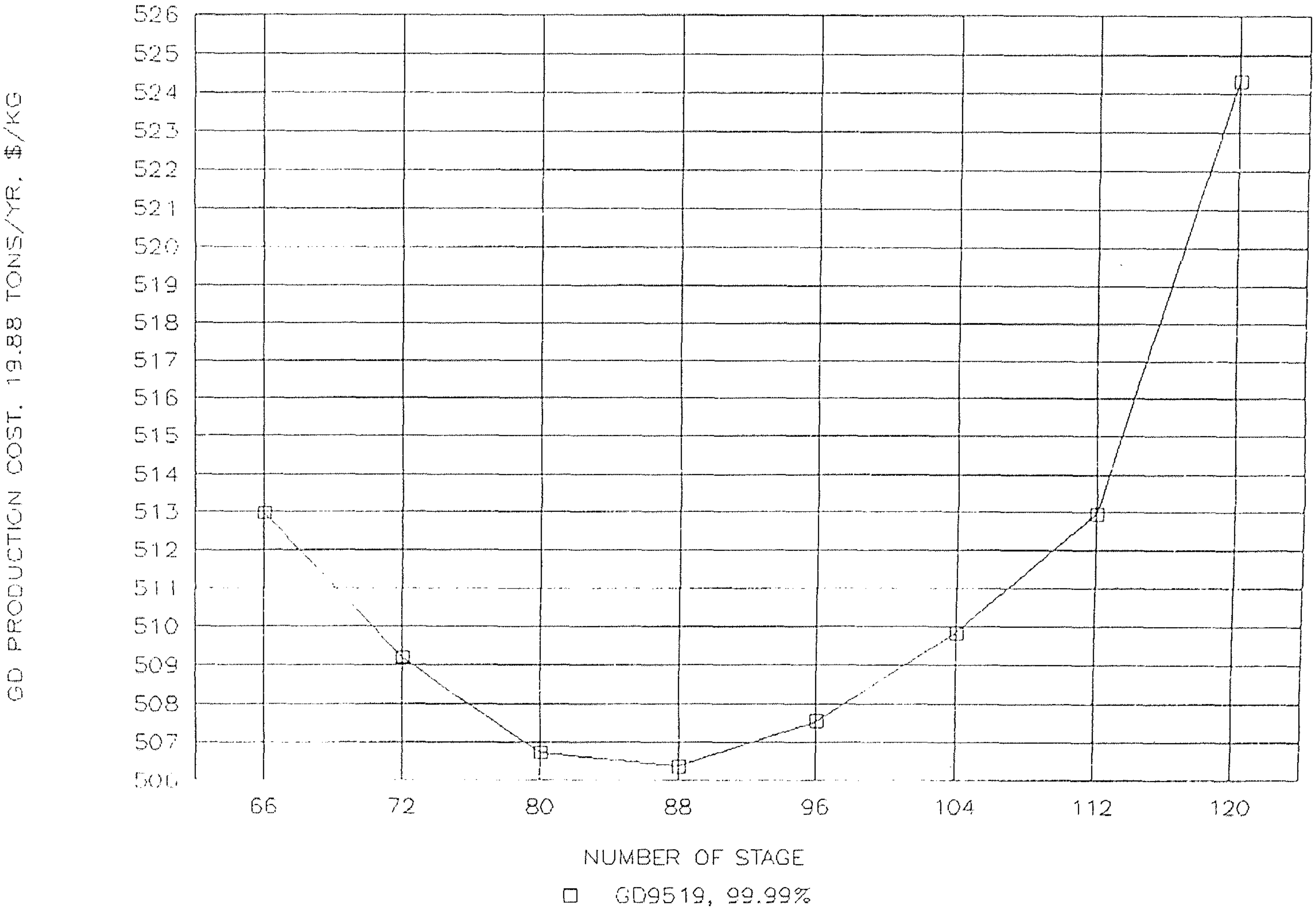

Figure 8.1 The Effect of Number of Stages on the Cost of Separation Gadolinium from the Sub-group Gd-La.

99.99% purity yttrium, or 102 mixer-settlers for 99.999% purity yttrium product.

As we examine Table 8.2, it clearly shows that as the ratio of extractant to feed increased, the costs for europium oxide purification decrease accordingly. However, Table 8.2 also shows, as the acidity in the aqueous phase increased, the costs decrease even more rapidly. Therefore, for the separation and purification of europium oxide in the HNO_3-H_2O-TBP system, the acidity in the aqueous phase is more influential than the extractant to the feed ratio in determining the cost of operations.

The behaviors of the yttrium oxide purification costs are quite different. Table 8.4 shows at 99.9% yttrium purity, as the ratio of extractant to feed increased, the costs for yttrium oxide purification decrease. However, at 99.999% yttrium purity, as the ratio of extractant to feed increased, the costs for yttrium oxide purification increase as well. Perhaps it is because the yttrium oxide did not transfer to the organic phase by extraction and remained in the aqueous solution. As the extractant to the feed ratio increased, more Lu and Yb were extracted, thus 99.9% yttrium oxide purity can be easily reached by fewer number of stages. For the 99.999% yttrium purity case, a large number of stages are required. As the ratio of extractant to feed increased, more yttrium along with lutetium and ytterbium were extracted into the organic phase, as a result, less yttrium oxide remained in the aqueous phase for recovery. Thus, the operation cost increases.

Since the acidity in the aqueous phase is more dominative than other factors in the total production costs for the europium separation and purification operations, one might thank it is wise to optimize the operation conditions by adjusting the acidity alone. As we discussed in Chapter 5, when the acidity in the aqueous phase was changed, higher or lower extractant to feed ratio is required. However, an extremely large or small ratio of the extractant to the feed will cause troubles in the practical operation.

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS

9.1 Conclusions

A mathematical model for the liquid-liquid equilibrium of the lanthanide and yttrium oxides in the nitric acid - water - tributyl phosphate (HNO_3-H_2O-TBP) two-phase system has been developed. All 16 rare earth distribution coefficients in this two-phase system which were experimentally determined by UK Harwell Laboratory were used to evaluate the parameters of this equilibrium model by a non-linear optimization technique. The uniquenesses of this model are:

1. This model is based on the inter-relationships of chemical reactions, phase equilibrium, and material balance. The chemical reactions were modelled using experimentally derived empirical equations for component involved. No heat of reaction or energy balance is considered in this model. Because model parameters were evaluated by solving non-linear simultaneous equations, therefore, once the numerical values of model parameters are determined, all concentration of species in the two-phase system are obtained simultaneously.

2. Most of the published liquid-liquid equilibrium models have a very narrow prediction range. Unlike other models, the model developed by this research has the capability of predicting the distribution coefficients for

all 16 rare earth oxides in the HNO_3-H_2O-TBP two-phase system for a acidity range of 0.3 to 16 N.

3. Because of the long range prediction capability, this model has practical value. This model can be used not only for predicting the liquid-liquid equilibrium in the laboratories, it also be used in actual process design for liquid-liquid extraction systems.

Based on the developed theoretical liquid-liquid equilibrium model, the optimum design of the liquid-liquid extraction systems in terms of capital investment and operating costs were analyzed for the following operations: (1) separation of gadolinium from the sub-group Gd-La of the lanthanide and yttrium oxides mineral sample; (2) separation and purification of europium from the sub-group Eu-La of the lanthanide and yttrium oxides mineral sample; and (3) purification of yttrium oxide from the mixture of lutetium, ytterbium and yttrium.

9.2 Suggestions

For further development of this mathematical liquid-liquid equilibrium model in the future, the following suggestions were made:

1. Incorporation of the macro-quantities of the initial rare earth concentrations into this model. Recall the extraction mechanism equation (2.3):

$$(M^{+3})_A + 3(NO_3^{-1})_A + 3(TBP)_O = (M(NO_3)_3(TBP)_3)_O \quad (2.3)$$

where $(M^{+3})_A$ and $(NO_3^{-1})_A$ represent the rare earth ion and nitrate in the aqueous phase, respectively. Consequently, the distributions of rare earth between the organic and aqueous phases are determined by two independent variables: the rare earth and acid concentrations in the aqueous phase, if the solvent concentration is fixed. The Harwell Laboratory experimental data in which our model were fitted into was determined in trace amounts of lanthanide and yttrium in the aqueous phase (<1 g/l). Therefore, if the initial rare earth concentrations are macro-quantities, the model may fail in predicting the distribution coefficients.

2. Conducting systematic investigations for the effect of feed stage location on the liquid-liquid extraction performance. Research efforts can also be focused on the effect of the feed concentration on the capital investment and operating costs.

3. Development of a liquid-liquid equilibrium model for predicting the simultaneous distribution of lanthanide and yttrium nitrates and nitric acid in the HNO_3-H_2O-TBP two-phase system. A few publications have already addressed the issue of competitive extraction by TBP (75), (76), (77), (78).

APPENDIX A

Tables

Table 5.2 The Calculated Distribution Coefficients of Yttrium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.71	0.0440	0.0438	0.3881	6.728000E-04	0.9920	0.3850
2	1.52	0.1000	0.1194	0.8196	4.360000E-04	0.9810	0.8040
3	3.23	0.2700	0.2889	1.8284	2.091000E-04	0.9492	1.7356
4	4.84	0.6400	0.5441	2.8978	1.584000E-04	0.9075	2.6297
5	6.55	1.1000	1.1237	4.1396	2.119000E-04	0.8497	3.5174
6	7.14	1.3800	1.4665	4.5887	2.285000E-04	0.8267	3.7935
7	7.83	2.2000	2.0270	5.1244	2.464000E-04	0.7980	4.0891
8	9.10	3.6000	3.9115	6.1320	2.736000E-04	0.7407	4.5417
9	10.40	9.0000	8.7673	7.1818	2.931000E-04	0.6774	4.8645
10	13.10	62.0000	62.0520	9.3794	3.042000E-04	0.5383	5.0483
11	15.00	220.0000	219.9795	10.9046	2.898000E-04	0.4411	4.8098

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	HOH
1	0.3890	0.0029	0.3145	0.0001	6.447780E-03	3.3810	1.1287
2	0.8100	0.0009	0.6911	0.0001	8.726610E-03	3.3373	2.1436
3	1.7422	0.0002	1.3916	0.0001	9.036920E-03	3.2619	3.4982
4	2.6372	0.0001	1.9313	0.0001	1.037298E-02	3.2090	4.2854
5	3.5333	0.0001	2.3913	0.0001	1.855815E-02	3.1651	4.4851
6	3.8125	0.0001	2.5291	0.0001	2.158598E-02	3.1513	4.9743
7	4.1117	0.0001	2.6799	0.0001	2.508110E-02	3.1352	5.1092
8	4.5703	0.0001	2.9364	0.0001	3.094055E-02	3.1046	5.2903
9	4.8978	0.0001	3.1820	0.0001	3.549504E-02	3.0709	5.4046
10	5.0843	0.0001	3.6817	0.0001	3.822799E-02	2.9916	5.5109
11	4.8421	0.0001	4.0601	0.0001	3.470126E-02	2.9273	5.5438

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.3 The Calculated Distribution Coefficients of Ytterbium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.33	0.0087	0.0078	0.1809	1.080000E-05	0.9968	0.1803
2	0.69	0.0260	0.0451	0.3791	1.201100E-03	0.9923	0.3761
3	1.26	0.0730	0.1346	0.6787	1.168000E-03	0.9848	0.6684
4	1.95	0.1630	0.2576	1.0611	9.342000E-04	0.9741	1.0336
5	2.92	0.4200	0.4377	1.6356	6.594000E-04	0.9559	1.5634
6	3.90	0.7100	0.6470	2.2596	5.083000E-04	0.9333	2.1090
7	5.13	1.2000	1.0303	3.1020	3.359000E-04	0.8986	2.7876
8	5.96	1.5300	1.4528	3.7037	3.888000E-04	0.8712	3.2267
9	6.95	2.1000	2.2876	4.4506	2.237000E-04	0.8344	3.7135
10	8.10	4.0000	4.0957	5.3488	2.535000E-04	0.7865	4.2068
11	9.36	8.2000	8.2320	6.3580	2.792000E-04	0.7289	4.6343
12	10.40	15.4000	15.2504	7.2022	2.943000E-04	0.6782	4.8844
13	11.00	22.0000	21.9930	7.6909	3.003000E-04	0.6480	4.9839
14	13.00	74.0000	74.0502	9.3199	3.060000E-04	0.5450	5.0791
15	15.00	220.0000	219.9870	10.9236	2.914000E-04	0.4427	4.8362

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.1879	0.0001	0.1382	0.0100	1.463000E-05	3.4485	1.0000
2	0.3777	0.0053	0.3060	0.0001	3.374880E-03	3.3821	1.1023
3	0.6724	0.0029	0.5739	0.0001	5.832400E-03	3.3507	1.8576
4	1.0392	0.0015	0.8800	0.0002	7.213940E-03	3.3162	2.5643
5	1.5701	0.0007	1.2744	0.0004	7.702200E-03	3.2739	3.3105
6	2.1162	0.0004	1.6298	0.0005	8.009210E-03	3.2381	3.8764
7	2.7953	0.0002	2.0170	0.0006	6.996280E-03	3.2009	4.4119
8	3.2346	0.0001	2.2450	0.0007	9.373970E-03	3.1793	4.6915
9	3.7216	0.0001	2.4879	0.0008	6.207880E-03	3.1555	4.9553
10	4.2152	0.0001	2.7395	0.0009	7.966730E-03	3.1285	5.1805
11	4.6424	0.0001	2.9905	0.0005	9.668180E-03	3.0976	5.3320
12	4.8924	0.0001	3.1865	0.0001	1.073986E-02	3.0703	5.4060
13	4.9924	0.0001	3.2973	0.0001	1.118188E-02	3.0537	5.4408
14	5.0880	0.0001	3.6678	0.0001	1.161315E-02	2.9939	5.5092
15	4.8440	0.0001	4.0652	0.0001	1.052894E-02	2.9266	5.5442

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.4 The Calculated Distribution Coefficients of Thulium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.58	0.0270	0.0183	0.3148	2.878000E-04	0.9938	0.3128
2	1.28	0.0760	0.0660	0.6887	6.719000E-04	0.9845	0.6780
3	2.43	0.1700	0.1741	1.3398	3.663000E-04	0.9656	1.2937
4	2.72	0.2300	0.2109	1.5135	3.085000E-04	0.9600	1.4529
5	3.70	0.3900	0.3773	2.1289	2.828000E-04	0.9383	1.9975
6	4.74	0.6500	0.6502	2.8284	1.822000E-04	0.9104	2.5751
7	7.38	2.0000	2.1174	4.7768	2.762000E-04	0.8170	3.9024
8	8.30	3.2000	3.2085	5.4981	3.025000E-04	0.7774	4.2742
9	9.22	5.4000	5.1279	6.2326	3.242000E-04	0.7350	4.5809
10	10.40	10.0000	10.2845	7.1867	3.445000E-04	0.6774	4.8679
11	11.10	16.2000	16.0862	7.7562	3.524000E-04	0.6419	4.9787
12	14.00	97.0000	97.0071	10.1116	3.519000E-04	0.4917	4.9717

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3279	0.0013	0.2468	0.0059	1.589960E-03	3.3924	1.0000
2	0.6835	0.0014	0.5824	0.0001	8.044470E-03	3.3497	1.8789
3	1.3002	0.0004	1.0803	0.0001	8.368290E-03	3.2944	2.9585
4	1.4596	0.0003	1.1965	0.0002	7.915940E-03	3.2821	3.1702
5	2.0044	0.0002	1.5609	0.0002	9.975010E-03	3.2449	3.7661
6	2.5822	0.0001	1.9011	0.0003	8.288920E-03	3.2119	4.2506
7	3.9188	0.0001	2.5835	0.0001	1.903590E-02	3.1456	5.0252
8	4.2945	0.0001	2.7784	0.0001	2.283598E-02	3.1240	5.1863
9	4.6047	0.0001	2.9605	0.0001	2.623080E-02	3.1015	5.3039
10	4.8951	0.0001	3.1830	0.0001	2.962056E-02	3.0708	5.4048
11	5.0073	0.0001	3.3121	0.0001	3.098431E-02	3.0514	5.4448
12	5.0004	0.0001	3.8569	0.0001	3.089725E-02	2.9621	5.5284

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.5 The Calculated Distribution Coefficients of Erbium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.39	0.0280	0.0262	0.2115	1.570000E-05	0.9961	0.2106
2	0.79	0.0480	0.0908	0.4293	7.339000E-04	0.9910	0.4255
3	1.51	0.1490	0.2072	0.8140	4.792000E-04	0.9811	0.7987
4	2.05	0.2500	0.2916	1.1180	4.076000E-04	0.9724	1.0871
5	3.46	0.5800	0.5146	1.9743	2.795000E-04	0.9440	1.8637
6	4.10	0.7000	0.6276	2.3926	1.665000E-04	0.9282	2.2208
7	4.85	0.8800	0.7825	2.9042	1.975000E-04	0.9072	2.6346
8	4.89	0.8300	0.7917	2.9321	1.992000E-04	0.9060	2.6564
9	5.51	1.0000	0.9517	3.3716	2.241000E-04	0.8865	2.9888
10	6.33	1.1800	1.2308	3.9735	2.556000E-04	0.8579	3.4088
11	6.57	1.3100	1.3323	4.1535	2.644000E-04	0.8490	3.5262
12	7.30	1.5800	1.7175	4.7107	2.898000E-04	0.8203	3.8640
13	8.81	2.9000	3.1382	5.8981	3.337000E-04	0.7645	4.4499
14	9.67	4.8000	4.7111	6.5886	3.527000E-04	0.7138	4.7028
15	10.10	6.1000	5.8953	6.9362	3.603000E-04	0.6928	4.8053
16	12.90	33.0000	33.0530	9.2144	3.798000E-04	0.5497	5.0642
17	15.80	186.0000	186.0083	11.5292	3.483000E-04	0.4029	4.6449

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.2230	0.0001	0.1628	0.0100	7.142000E-05	3.4343	1.0000
2	0.4300	0.0023	0.3528	0.0001	6.706370E-03	3.3765	1.2478
3	0.8047	0.0008	0.6866	0.0001	8.218980E-03	3.3378	2.1337
4	1.0935	0.0005	0.9223	0.0001	9.516330E-03	3.3115	2.6492
5	1.8704	0.0002	1.4757	0.0001	1.118774E-02	3.2534	3.6320
6	2.2275	0.0001	1.6973	0.0001	7.942900E-03	3.2315	3.9637
7	2.6430	0.0001	1.9341	0.0001	1.117866E-02	3.2088	4.2890
8	2.6650	0.0001	1.9461	0.0001	1.136443E-02	3.2076	4.3054
9	3.0005	0.0001	2.1234	0.0001	1.438647E-02	3.1908	4.5305
10	3.4249	0.0001	2.3372	0.0001	1.871387E-02	3.1704	4.7790
11	3.5436	0.0001	2.3958	0.0001	2.002509E-02	3.1647	4.8420
12	3.8856	0.0001	2.5646	0.0001	2.404556E-02	3.1476	5.0099
13	4.4795	0.0001	2.8793	0.0001	3.189049E-02	3.1119	5.2571
14	4.7363	0.0001	3.0450	0.0001	3.561834E-02	3.0903	5.3489
15	4.8404	0.0001	3.1257	0.0001	3.718790E-02	3.0791	5.3842
16	5.1035	0.0001	3.6434	0.0001	4.130307E-02	2.9980	5.5066
17	4.6774	0.0001	4.2354	0.0001	3.474669E-02	2.8971	5.5538

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.6 The Calculated Distribution Coefficients of Holmium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.72	0.0710	0.0645	0.3932	9.654000E-04	0.9919	0.3901
2	1.23	0.1290	0.1417	0.6619	7.825000E-04	0.9852	0.6521
3	3.31	0.4200	0.4441	1.8764	2.667000E-04	0.9475	1.7780
4	4.10	0.6000	0.5571	2.3895	1.663000E-04	0.9283	2.2182
5	5.15	0.7300	0.7182	3.1128	2.096000E-04	0.8982	2.7958
6	7.47	1.3000	1.3388	4.8465	2.955000E-04	0.8131	3.9405
7	8.47	1.9900	2.0309	5.6341	3.251000E-04	0.7694	4.3350
8	9.45	3.5000	3.4208	6.4200	3.483000E-04	0.7235	4.6444
9	11.10	9.3000	9.3260	7.7596	3.730000E-04	0.6410	4.9737
10	14.00	47.0000	47.0004	10.1149	3.723000E-04	0.4909	4.9649

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3942	0.0033	0.3193	0.0004	5.453250E-03	3.3805	1.1468
2	0.6573	0.0016	0.5596	0.0001	7.388190E-03	3.3523	1.8206
3	1.7885	0.0002	1.4197	0.0020	6.865670E-03	3.2590	3.5954
4	2.2295	0.0001	1.6958	0.0024	5.343070E-03	3.2316	4.0262
5	2.8082	0.0001	2.0215	0.0023	8.487930E-03	3.2005	4.4670
6	3.9576	0.0001	2.6032	0.0010	1.686135E-02	3.1434	5.0693
7	4.3545	0.0001	2.8132	0.0006	2.040647E-02	3.1197	5.2253
8	4.6661	0.0001	3.0052	0.0003	2.342335E-02	3.0954	5.3318
9	4.9983	0.0001	3.3129	0.0001	2.686265E-02	3.0510	5.4426
10	4.9893	0.0001	3.8577	0.0001	2.676768E-02	2.9617	5.5266

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.7 The Calculated Distribution Coefficients of Terbium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	1.36	0.2100	0.1601	0.7317	4.065000E-04	0.9834	0.7195
2	2.55	0.3900	0.3082	1.4111	1.538000E-04	0.9633	1.3594
3	4.29	0.5700	0.5300	2.5138	2.621000E-04	0.9231	2.3203
4	4.95	0.7000	0.6205	2.9642	3.027000E-04	0.9040	2.6794
5	5.80	0.7200	0.7457	3.5680	3.532000E-04	0.8762	3.1258
6	5.83	0.7300	0.7503	3.5898	3.549000E-04	0.8752	3.1411
7	7.05	0.8700	0.9572	4.4976	4.210000E-04	0.8287	3.7262
8	7.10	0.8500	0.9668	4.5357	4.235000E-04	0.8266	3.7484
9	8.10	1.1900	1.1911	5.3085	4.695000E-04	0.7831	4.1556
10	9.15	1.5500	1.5727	6.1389	5.083000E-04	0.7332	4.4990
11	9.77	2.0000	1.9607	6.6359	5.262000E-04	0.7021	4.6569
12	10.60	3.0000	2.8741	7.3065	5.439000E-04	0.6592	4.8141
13	12.30	8.2000	8.0892	8.6893	5.586000E-04	0.5692	4.9440
14	13.00	12.7000	12.8766	9.2598	5.566000E-04	0.5323	4.9264
15	16.30	53.0000	52.9787	11.1089	5.218000E-04	0.4159	4.6185

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.7259	0.0005	0.6186	0.0001	9.059400E-03	3.3456	1.9692
2	1.3661	0.0001	1.1288	0.0001	6.467880E-03	3.2892	3.0470
3	2.3366	0.0001	1.7567	0.0001	1.884327E-02	3.2257	4.0479
4	2.7023	0.0001	1.9599	0.0001	2.512714E-02	3.2063	4.3229
5	3.1582	0.0001	2.1968	0.0001	3.419718E-02	3.1839	4.6172
6	3.1738	0.0001	2.2047	0.0001	3.453278E-02	3.1832	4.6265
7	3.7737	0.0001	2.5025	0.0001	4.859598E-02	3.1540	4.9490
8	3.7965	0.0001	2.5139	0.0001	4.917675E-02	3.1529	4.9600
9	4.2157	0.0001	2.7296	0.0001	6.044153E-02	3.1297	5.1499
10	4.5700	0.0001	2.9387	0.0001	7.084350E-02	3.1044	5.2923
11	4.7332	0.0001	3.0566	0.0001	7.590351E-02	3.0888	5.3539
12	4.8958	0.0001	3.2109	0.0001	8.111445E-02	3.0668	5.4153
13	5.0301	0.0001	3.5234	0.0001	8.555097E-02	3.0179	5.4896
14	5.0118	0.0001	3.6541	0.0001	8.494295E-02	2.9963	5.5079
15	4.6927	0.0001	4.1156	0.0001	7.465689E-02	2.9178	5.5472

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.8 The Calculated Distribution Coefficients of Dysprosium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.30	0.0310	0.0183	0.1656	1.320000E-05	0.9971	0.1651
2	0.78	0.0840	0.0890	0.4238	5.713000E-04	0.9912	0.4201
3	1.09	0.1230	0.1339	0.5865	4.632000E-04	0.9871	0.5790
4	2.05	0.2500	0.2661	1.1179	2.608000E-04	0.9724	1.0870
5	2.64	0.3500	0.3440	1.4652	2.254000E-04	0.9616	1.4088
6	3.67	0.5100	0.4780	2.1094	1.584000E-04	0.9390	1.9807
7	4.90	0.6700	0.6436	2.9346	2.126000E-04	0.9057	2.6576
8	5.90	0.8300	0.7997	3.6484	2.548000E-04	0.8731	3.1850
9	6.84	0.9900	0.9878	4.3489	2.915000E-04	0.8380	3.6439
10	7.78	1.1600	1.2557	5.0721	3.241000E-04	0.7989	4.0516
11	9.54	2.3000	2.3013	6.4684	3.708000E-04	0.7168	4.6357
12	10.50	3.7000	3.6550	7.2441	3.872000E-04	0.6685	4.8412
13	13.10	19.5000	19.5124	9.3600	3.985000E-04	0.5323	4.9813
14	16.60	174.0000	174.0049	12.1299	3.486000E-04	0.3593	4.3576

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.1705	0.0001	0.1257	0.0100	6.814000E-05	3.4557	1.0000
2	0.4252	0.0017	0.3477	0.0001	7.500570E-03	3.3771	1.2304
3	0.5848	0.0010	0.4943	0.0001	8.381020E-03	3.3599	1.6487
4	1.0936	0.0003	0.9222	0.0001	8.861760E-03	3.3115	2.6486
5	1.4155	0.0002	1.1648	0.0001	9.923580E-03	3.2854	3.1121
6	1.9877	0.0001	1.5503	0.0001	9.807930E-03	3.2459	3.7468
7	2.6726	0.0001	1.9472	0.0001	1.765709E-02	3.2075	4.3062
8	3.2080	0.0001	2.2256	0.0001	2.536058E-02	3.1812	4.6507
9	3.6750	0.0001	2.4571	0.0001	3.319501E-02	3.1586	4.9035
10	4.0908	0.0001	2.6659	0.0001	4.103865E-02	3.1367	5.0978
11	4.6881	0.0001	3.0169	0.0001	5.372428E-02	3.0941	5.3341
12	4.8986	0.0001	3.1963	0.0001	5.859304E-02	3.0689	5.4099
13	5.0420	0.0001	3.6772	0.0001	6.203337E-02	2.9924	5.5104
14	4.4031	0.0001	4.4221	0.0001	4.747169E-02	2.8644	5.5602

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.9 The Calculated Distribution Coefficients of Gadolinium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.72	0.1080	0.0859	0.3928	9.253000E-04	0.9920	0.3896
2	1.29	0.1930	0.1661	0.6938	5.978000E-04	0.9847	0.6832
3	2.31	0.3100	0.2891	1.2689	3.070000E-04	0.9680	1.2283
4	2.94	0.3700	0.3562	1.6478	3.936000E-04	0.9556	1.5746
5	3.56	0.4200	0.4172	2.0383	2.399000E-04	0.9417	1.9194
6	4.58	0.4900	0.5073	2.7139	3.104000E-04	0.9150	2.4832
7	5.47	0.5200	0.5764	3.3370	3.702000E-04	0.8876	2.9617
8	6.40	0.6300	0.6418	4.0177	4.292000E-04	0.8547	3.4336
9	7.54	0.7000	0.7275	4.8855	4.938000E-04	0.8088	3.9507
10	8.67	0.9500	0.8763	5.7727	5.467000E-04	0.7579	4.3741
11	9.40	1.1400	1.0725	6.3559	5.739000E-04	0.7226	4.5919
12	10.60	1.7000	1.8033	7.3254	6.058000E-04	0.6618	4.8468
13	12.20	4.6000	4.5619	8.6280	6.228000E-04	0.5777	4.9831
14	13.70	11.0000	11.0097	9.8466	6.138000E-04	0.4989	4.9110
15	15.30	25.0000	25.0022	11.1253	5.814000E-04	0.4182	4.6519

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3946	0.0019	0.3189	0.0100	7.209930E-03	3.3805	1.1422
2	0.6893	0.0007	0.5867	0.0001	8.168330E-03	3.3492	1.8897
3	1.2350	0.0002	1.0311	0.0001	7.543600E-03	3.2997	2.8647
4	1.5815	0.0002	1.2821	0.0002	1.239682E-02	3.2731	3.3182
5	1.9263	0.0001	1.5115	0.0002	9.210240E-03	3.2498	3.6897
6	2.4960	0.0001	1.8500	0.0001	1.541570E-02	3.2168	4.1767
7	2.9813	0.0001	2.1103	0.0001	2.192916E-02	3.1921	4.5129
8	3.4609	0.0001	2.3519	0.0001	2.947402E-02	3.1690	4.7929
9	3.9880	0.0001	2.6144	0.0001	3.902007E-02	3.1423	5.0532
10	4.4205	0.0001	2.8483	0.0001	4.783187E-02	3.1157	5.2355
11	4.6435	0.0001	2.9902	0.0001	5.271386E-02	3.0977	5.3203
12	4.9046	0.0001	3.2148	0.0001	5.872867E-02	3.0661	5.4160
13	5.0441	0.0001	3.5090	0.0001	6.207821E-02	3.0202	5.4867
14	4.9700	0.0001	3.7923	0.0001	6.029480E-02	2.9730	5.5224
15	4.7043	0.0001	4.1200	0.0001	5.410043E-02	2.9170	5.5472

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.10 The Calculated Distribution Coefficients of Europium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.64	0.1050	0.1362	0.3513	9.250000E-04	0.9929	0.3488
2	1.67	0.3000	0.2759	0.9022	3.602000E-04	0.9786	0.8830
3	2.38	0.3900	0.3443	1.3097	2.582000E-04	0.9665	1.2658
4	3.76	0.4900	0.4491	2.1614	4.130000E-04	0.9369	2.0249
5	5.38	0.5300	0.5423	3.2587	5.919000E-04	0.0891	2.9017
6	6.11	0.5400	0.5767	3.7840	6.680000E-04	0.8658	3.2747
7	6.30	0.5400	0.5852	3.9234	6.871000E-04	0.8589	3.3682
8	7.22	0.5800	0.6269	4.6126	7.740000E-04	0.8231	3.7946
9	7.27	0.5900	0.6293	4.6507	7.785000E-04	0.8211	3.8163
10	8.46	0.7300	0.7110	5.5717	8.738000E-04	0.7694	4.2836
11	8.92	0.7600	0.7663	5.9343	9.048000E-04	0.7480	4.4356
12	9.35	0.8900	0.8409	6.2759	9.306000E-04	0.7275	4.5621
13	10.40	1.2600	1.1822	7.1184	9.800000E-04	0.6755	4.8042
14	12.50	3.4000	3.4332	8.8238	1.019400E-03	0.5669	4.9972
15	16.00	19.9000	19.8986	11.6338	9.257000E-04	0.3904	4.5381

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3543	0.0013	0.2798	0.0001	7.447900E-03	3.3852	1.0194
2	0.8900	0.0002	0.7574	0.0003	7.343260E-03	3.3298	2.3002
3	1.2732	0.0001	1.0596	0.0004	7.545150E-03	3.2966	2.9262
4	2.0419	0.0001	1.5784	0.0001	1.930834E-02	3.2431	3.7892
5	2.9403	0.0001	2.0802	0.0001	3.964997E-02	3.1950	4.4761
6	3.3249	0.0001	2.2738	0.0001	5.049878E-02	3.1766	4.7065
7	3.4216	0.0001	2.3213	0.0001	5.342366E-02	3.1720	4.7597
8	3.8635	0.0001	2.5373	0.0001	6.780627E-02	3.1505	4.9826
9	3.8861	0.0001	2.5484	0.0001	6.858401E-02	3.1493	4.9932
10	4.3727	0.0001	2.7990	0.0001	8.640835E-02	3.1216	5.2018
11	4.5316	0.0001	2.8899	0.0001	9.264941E-02	3.1106	5.2629
12	4.6638	0.0001	2.9729	0.0001	9.800935E-02	3.1000	5.3114
13	4.9175	0.0001	3.1695	0.0001	1.086876E-01	3.0728	5.4006
14	5.1198	0.0001	3.5554	0.0001	1.175957E-01	3.0126	5.4944
15	4.6375	0.0001	4.2672	0.0001	9.698086E-02	2.8915	5.5551

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.11 The Calculated Distribution Coefficients of Samarium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.59	0.0770	0.0622	0.3208	8.158000E-04	0.9936	0.3187
2	1.04	0.2100	0.1285	0.5598	1.238700E-03	0.9878	0.5530
3	2.24	0.3800	0.2807	1.2279	7.616000E-04	0.9691	1.1900
4	3.25	0.4200	0.3805	1.8400	5.586000E-04	0.9489	1.7459
5	4.48	0.4400	0.4635	2.6414	7.757000E-04	0.9179	2.4243
6	5.06	0.4560	0.4874	3.0405	8.762000E-04	0.9007	2.7383
7	5.96	0.4500	0.5063	3.6839	1.026200E-03	0.8707	3.2069
8	7.01	0.4600	0.5080	4.4666	1.186700E-03	0.8305	3.7087
9	7.97	0.5000	0.5102	5.2061	1.314500E-03	0.7893	4.1079
10	9.04	0.6000	0.5584	6.0503	1.430200E-03	0.7391	4.4696
11	10.30	0.8300	0.7829	7.0625	1.525900E-03	0.6755	4.7686
12	11.00	1.0800	1.0479	7.6301	1.559400E-03	0.6390	4.8732
13	11.30	1.1600	1.2039	7.8740	1.569500E-03	0.6232	4.9047
14	13.90	4.1000	4.1170	9.9881	1.556700E-03	0.4873	4.8647
15	15.70	8.2000	8.1928	11.4216	1.457600E-03	0.3990	4.5552

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3325	0.0008	0.2521	0.0048	2.843950E-03	3.3910	1.0000
2	0.5591	0.0007	0.4707	0.0001	7.492320E-03	3.2626	1.5847
3	1.1967	0.0002	1.0020	0.0001	9.912700E-03	3.3028	2.8079
4	1.7541	0.0001	1.3985	0.0001	1.066858E-02	3.2612	3.5092
5	2.4430	0.0001	1.8168	0.0001	2.057030E-02	3.2199	4.1315
6	2.7629	0.0001	1.9919	0.0001	2.624400E-02	3.2033	4.3643
7	3.2418	0.0001	2.2384	0.0001	3.599472E-02	3.1800	4.6658
8	3.7565	0.0001	2.4932	0.0001	4.814059E-02	3.1550	4.9399
9	4.1674	0.0001	2.7025	0.0001	5.906194E-02	3.1327	5.1284
10	4.5406	0.0001	2.9172	0.0001	6.992063E-02	3.1072	5.2798
11	4.8498	0.0001	3.1553	0.0001	7.958841E-02	3.0749	5.3956
12	4.9581	0.0001	3.2843	0.0001	8.311827E-02	3.0558	5.4381
13	4.9907	0.0001	3.3393	0.0001	8.419628E-02	3.0473	5.4527
14	4.9488	0.0001	3.8269	0.0001	8.282857E-02	2.9672	5.5261
15	4.6284	0.0001	4.2040	0.0001	7.262446E-02	2.9025	5.5522

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.12 The Calculated Distribution Coefficients of Promethium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.36	0.0530	0.0686	0.1961	4.840000E-05	0.9964	0.1954
2	0.70	0.1270	0.1493	0.3820	1.693600E-03	0.9922	0.3794
3	1.18	0.2200	0.2230	0.6340	1.241100E-03	0.9859	0.6256
4	2.16	0.3100	0.3061	1.1803	8.529000E-04	0.9705	1.1465
5	2.99	0.3600	0.3418	1.6773	3.972000E-04	0.9545	1.6020
6	4.04	0.3900	0.3630	2.3476	5.420000E-04	0.9297	2.1856
7	5.37	0.3600	0.3855	3.2591	7.213000E-04	0.8908	2.9087
8	6.27	0.3400	0.3581	3.9120	8.356000E-04	0.8595	3.3695
9	7.03	0.3300	0.3501	4.4822	9.247000E-04	0.8300	3.7287
10	7.94	0.3300	0.3457	5.1835	1.019500E-03	0.7912	4.1110
11	9.24	0.3700	0.3759	6.2114	1.127600E-03	0.7304	4.5470
12	10.40	0.5300	0.4875	7.1459	1.193300E-03	0.6720	4.8119
13	10.80	0.5700	0.5568	7.4705	1.208900E-03	0.6512	4.8748
14	13.00	1.4100	1.4150	9.2631	1.231200E-03	0.5352	4.9648
15	15.80	4.3000	4.2697	11.5043	1.125100E-03	0.3940	4.5367

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.2055	0.0001	0.1505	0.0100	9.545000E-05	3.4414	1.0000
2	0.3845	0.0018	0.3092	0.0001	6.477490E-03	3.3817	1.1121
3	0.6317	0.0008	0.5361	0.0001	7.827500E-03	3.3551	1.7596
4	1.1533	0.0003	0.9686	0.0002	9.858460E-03	3.3065	2.7444
5	1.6091	0.0001	1.3011	0.0003	6.416010E-03	3.2712	3.3535
6	2.1951	0.0001	1.6764	0.0001	1.194211E-02	3.2335	3.9335
7	2.9278	0.0001	2.0824	0.0001	2.115133E-02	3.1947	4.4786
8	3.3962	0.0001	2.3197	0.0001	2.838382E-02	3.1721	4.7576
9	3.7620	0.0001	2.5008	0.0001	3.475800E-02	3.1542	4.9470
10	4.1523	0.0001	2.6995	0.0001	4.225080E-02	3.1330	5.1254
11	4.5981	0.0001	2.9595	0.0001	5.168802E-02	3.1017	5.3035
12	4.8694	0.0001	3.1777	0.0001	5.788595E-02	3.0716	5.4030
13	4.9339	0.0001	3.2515	0.0001	5.940918E-02	3.0606	5.4276
14	5.0259	0.0001	3.6582	0.0001	6.162309E-02	2.9955	5.5078
15	4.5870	0.0001	4.2313	0.0001	5.145411E-02	2.8977	5.5530

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.13 The Calculated Distribution Coefficients of Neodymium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.53	0.0500	0.0817	0.2837	2.250000E-05	0.9945	0.2821
2	0.86	0.1580	0.1498	0.4651	9.946000E-04	0.9902	0.4605
3	1.40	0.2300	0.2203	0.7520	7.094000E-04	0.9828	0.7890
4	2.36	0.2900	0.2811	1.2950	4.007000E-04	0.9670	1.2523
5	3.12	0.3200	0.3003	1.7550	2.672000E-04	0.9518	1.6704
6	4.47	0.3300	0.3048	2.6364	1.936000E-04	0.9184	2.4212
7	5.31	0.2800	0.2964	3.2219	2.302000E-04	0.8932	2.8780
8	6.22	0.2400	0.2817	3.8846	2.679000E-04	0.8622	3.3490
9	7.16	0.2400	0.2642	4.5948	3.036000E-04	0.8260	3.7950
10	8.09	0.2400	0.2503	5.3175	3.345000E-04	0.7864	4.1815
11	9.53	0.2700	0.2565	6.4643	3.718000E-04	0.7191	4.6476
12	10.60	0.3300	0.3100	7.3319	3.901000E-04	0.6653	4.8772
13	11.40	0.4200	0.3968	7.9838	3.984000E-04	0.6240	4.9810
14	12.40	0.5800	0.5855	8.7990	4.024000E-04	0.5719	5.0311
15	13.20	0.8500	0.8187	9.4491	4.008000E-04	0.5303	5.0104
16	14.30	1.2500	1.2834	10.3383	3.919000E-04	0.4739	4.8988
17	15.10	1.7000	1.7330	10.9764	3.810000E-04	0.4340	4.7634
18	15.90	2.3000	2.2700	11.6032	3.670000E-04	0.3955	4.5887

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3052	0.0001	0.2199	0.0100	7.181000E-05	3.4015	1.0000
2	0.4665	0.0027	0.3856	0.0001	5.166970E-03	3.3726	1.3564
3	0.7482	0.0012	0.6355	0.0019	5.914030E-03	3.3436	2.0452
4	1.2646	0.0004	1.0493	0.0030	5.660980E-03	3.2977	2.9712
5	1.6842	0.0002	1.3478	0.0037	5.035980E-03	3.2664	3.5237
6	2.4371	0.0001	1.8144	0.0046	5.290230E-03	3.2202	4.2582
7	2.8974	0.0001	2.0653	0.0050	7.474720E-03	3.1963	4.6036
8	3.3737	0.0001	2.3075	0.0058	1.012147E-02	3.1732	4.9171
9	2.8262	0.0001	2.5309	0.0070	1.299681E-02	3.1509	5.1849
10	4.2196	0.0001	2.7314	0.0083	1.577893E-02	3.1291	5.3974
11	4.6949	0.0001	3.0157	0.0010	1.949265E-02	3.0937	5.6230
12	4.9265	0.0001	3.2161	0.0010	2.146617E-02	3.0652	5.6938
13	5.0313	0.0001	3.3634	0.0010	2.238961E-02	3.0426	5.7258
14	5.0818	0.0001	3.5478	0.0010	2.284227E-02	3.0129	5.7496
15	5.0607	0.0001	3.6980	0.0010	2.265470E-02	2.9881	5.7609
16	4.9446	0.0001	3.9132	0.0089	2.165673E-02	2.9518	5.7416
17	4.8048	0.0001	4.0793	0.0078	2.047611E-02	2.9235	5.7215
18	4.6253	0.0001	4.2672	0.0068	1.900171E-02	2.8929	5.7007

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.14 The Calculated Distribution Coefficients of Praseodymium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.34	0.0410	0.0438	0.1859	3.140000E-05	0.9967	0.1852
2	1.38	0.1640	0.1597	0.7419	6.193000E-04	0.9831	0.7294
3	2.58	0.2000	0.2033	1.4277	2.334000E-04	0.9629	1.3748
4	3.20	0.2200	0.2101	1.8079	2.917000E-04	0.9502	1.7178
5	4.13	0.2000	0.2082	2.4080	3.793000E-04	0.9278	2.2339
6	5.20	0.1910	0.1939	3.1404	4.782000E-04	0.8969	2.8164
7	6.16	0.1670	0.1762	3.8328	5.627000E-04	0.8647	3.3137
8	7.23	0.1520	0.1543	4.6372	6.483000E-04	0.8236	3.8179
9	8.54	0.1460	0.1414	5.6571	7.359000E-04	0.7664	4.3340
10	9.12	0.1590	0.1447	6.1177	7.675000E-04	0.7392	4.5199
11	10.00	0.1750	0.1654	6.8238	9.061000E-04	0.6961	4.7473
12	12.40	0.3300	0.3539	8.7731	8.526000E-04	0.5727	5.0209
13	15.10	0.8300	0.8225	10.9514	8.096000E-04	0.4356	4.7675

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.1938	0.0001	0.1422	0.0100	1.112900E-04	3.4462	1.0000
2	0.7370	0.0005	0.6272	0.0007	8.631580E-03	3.3446	2.0016
3	1.3838	0.0001	1.1399	0.0013	6.132910E-03	3.2880	3.0961
4	1.7271	0.0001	1.3795	0.0009	9.574870E-03	3.2631	3.5001
5	2.2477	0.0001	1.7050	0.0001	1.619255E-02	3.2307	3.9746
6	2.8401	0.0001	2.0329	0.0001	2.573810E-02	3.1994	4.4161
7	3.3479	0.0001	2.2902	0.0001	3.562987E-02	3.1749	4.7238
8	3.8647	0.0001	2.5439	0.0001	4.729737E-02	3.1495	4.9862
9	4.3955	0.0001	2.8199	0.0001	6.094888E-02	3.1186	5.2114
10	4.5872	0.0001	2.9339	0.0001	6.628962E-02	3.1044	5.2830
11	4.8219	0.0001	3.1008	0.0001	7.312759E-02	3.0818	5.3653
12	5.1046	0.0001	3.5430	0.0001	8.179958E-02	3.0136	5.4835
13	4.8420	0.0001	4.0732	0.0001	7.375124E-02	2.9244	5.5397

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.15 The Calculated Distribution Coefficients of Cerium and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.27	0.0280	0.0295	0.1504	2.440000E-05	0.9974	0.1500
2	0.72	0.0990	0.0990	0.3915	1.202600E-03	0.9919	0.3883
3	0.98	0.1230	0.1241	0.5263	9.328000E-04	0.9886	0.5203
4	1.82	0.1680	0.1642	0.9830	4.692000E-04	0.9764	0.9597
5	2.38	0.1720	0.1725	1.3054	4.113000E-04	0.9667	1.2619
6	3.64	0.1690	0.1664	2.0812	3.188000E-04	0.9399	1.9561
7	5.20	0.1330	0.1371	3.1282	4.567000E-04	0.8959	2.8020
8	6.00	0.1100	0.1192	3.7037	5.234000E-04	0.8673	3.2113
9	6.85	0.0980	0.1018	4.3390	5.880000E-04	0.8319	3.6077
10	8.15	0.0900	0.0856	5.3459	6.687000E-04	0.7682	4.1030
11	8.95	0.0960	0.0856	5.9814	7.056000E-03	0.7245	4.3292
12	9.88	0.1080	0.0981	6.7304	7.360000E-04	0.6717	4.5155
13	11.30	0.1330	0.1455	7.8860	7.589000E-04	0.5912	4.6562
14	13.90	0.2800	0.3144	10.0012	7.439000E-04	0.4568	4.5640
15	15.00	0.4200	0.4067	10.8802	7.206000E-04	0.4067	4.4212

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.1530	0.0001	0.1133	0.0100	4.300000E-05	3.4628	1.0000
2	0.3959	0.0019	0.3176	0.0140	5.475700E-03	3.3807	1.1546
3	0.5298	0.0011	0.4409	0.0020	5.691830E-03	3.3661	1.5316
4	0.9730	0.0003	0.8205	0.0034	5.281330E-03	3.3228	2.5098
5	1.2766	0.0002	1.0565	0.0041	6.087390E-03	3.2969	3.0129
6	1.9766	0.0001	1.5351	0.0054	7.313640E-03	3.2474	3.8718
7	2.8431	0.0001	2.0279	0.0094	1.500679E-02	3.1996	4.6915
8	3.2598	0.0001	2.2455	0.0100	1.971121E-02	3.1785	4.9733
9	3.6626	0.0001	2.4547	0.0100	2.487782E-02	3.1572	5.1913
10	4.1672	0.0001	2.7400	0.0100	3.217767E-02	3.1247	5.4221
11	4.3980	0.0001	2.9008	0.0100	3.582340E-02	3.1040	5.5148
12	4.5880	0.0001	3.0789	0.0100	3.897294E-02	3.0791	5.5888
13	4.7309	0.0001	3.3416	0.0100	4.143953E-02	3.0393	5.6575
14	4.6348	0.0001	3.8291	0.0100	3.981464E-02	2.9609	5.7225
15	4.4886	0.0001	4.0626	0.0100	3.736215E-02	2.9241	5.7409

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.16 The Calculated Distribution Coefficients of Lanthanum and Composition in Aqueous and Organic Phases.

Test	(HNO3)ai	Kd exp	Kd calc	(HNO3)at	(MNO3+2)a	Deg Ionz	(NO3-1)a
1	0.63	0.0740	0.0731	0.3472	1.599000E-03	0.9930	0.3448
2	1.21	0.1080	0.1098	0.6505	1.238700E-03	0.9855	0.6411
3	2.15	0.1230	0.1235	1.1748	7.344000E-04	0.9708	1.1403
4	3.17	0.1240	0.1184	1.7889	4.381000E-04	0.9507	1.7007
5	4.27	0.1020	0.1054	2.5041	2.979000E-04	0.9238	2.3132
6	6.10	0.0760	0.0794	3.8044	4.245000E-04	0.8663	3.2957
7	8.05	0.0570	0.0563	5.3028	5.384000E-04	0.7883	4.1802
8	10.20	0.0600	0.0539	7.0274	6.219000E-04	0.6871	4.8280
9	13.80	0.1420	0.1511	9.9539	6.433000E-04	0.5018	4.9945
10	15.00	0.2200	0.2122	10.9121	6.199000E-04	0.4410	4.8122

Test	(H+1)a	(M+3)a	(HNO3)o	(M)o	(M(NO3)2)a	(TBP)o	NOH
1	0.3483	0.0036	0.2760	0.0002	4.607340E-03	3.3856	1.0083
2	0.6474	0.0015	0.5498	0.0006	6.636770E-03	3.3535	1.8039
3	1.1486	0.0005	0.9637	0.0011	6.998770E-03	3.3070	2.7561
4	1.7103	0.0002	1.3682	0.0016	6.227290E-03	3.2643	3.5001
5	2.3238	0.0001	1.7519	0.0021	5.760230E-03	3.2262	4.0966
6	3.3079	0.0001	2.2801	0.0011	1.169255E-02	3.1759	4.7430
7	4.1967	0.0001	2.7275	0.0001	1.881083E-02	3.1298	5.1469
8	4.8510	0.0001	3.1466	0.0001	2.509276E-02	3.0759	5.3899
9	5.0193	0.0001	3.8184	0.0001	2.685332E-02	2.9684	5.5237
10	4.8349	0.0001	4.0621	0.0001	2.492879E-02	2.9269	5.5430

Initial Concentration:
TBP 3.66 M
Rare Earths 0.01 M

Table 5.18 The Effect of Number of Stages on Promethium Extraction HNO_3, 12.0 N.

% OF PROMETHIUM EXTRACTED

STAGE	CASE A	CASE B	CASE C
20	84,3153	94,3653	98,6706
25	87,5117	96,4835	99,3876
30	91,7250	98,3318	99,8110
35	93,6251	98,9834	99,9137
40	95,8179	99,5211	99,9734
45	96,8249	99,7099	99,9879
50	97,9270	99,8636	99,9963
55	98,4362	99,9175	99,9983
60	98,9811	99,9612	99,9995

Feed 12.0 N HNO_3 0.5 l/h, center feed
Rare Earth in feed 25.0 g/l
Solvent TBP equilibrated with 12.0 N HNO_3
case a: 15.73 l/h
case b: 17.52 l/h
case c: 20.14 l/h
Scrub 12.0 N HNO_3, 14.5 l/h

Table 5.19 The Effect of Number of Stages on Promethium Extraction HNO_3, 13.0 N.

% OF PROMETHIUM EXTRACTED

STAGE	CASE A	CASE B	CASE C
20	78,6974	92,0872	98,8533
25	81,6161	94,6407	99,4827
30	86,3914	97,1537	99,8451
35	88,6171	98,1258	99,9307
40	91,6375	99,0132	99,9793
45	93,1176	99,3558	99,9908
50	94,9677	99,6617	99,9972
55	95,8932	99,7798	99,9988
60	97,0048	99,8844	99,9996

Feed 13.0 N HNO_3 0.5 l/h, center feed
Rare Earth in feed 25.0 g/l
Solvent TBP equilibrated with 12.0 N HNO_3
    case a: 9.99 l/h
    case b: 11.14 l/h
    case c: 13.43 l/h
Scrub 13.0 N HNO_3, 14.5 l/h

Table 6.5 The Effect of Number of Stages on Europium Purification, HNO_3 9.8 N, TBP 2.5 l/h.

STAGE	% RECOVERY	% PURITY
42	80.5147	96.2548
48	81.5966	97.9642
54	82.4452	98.8972
60	83.1223	99.4034
66	83.6700	99.6774
72	84.1183	99.8255
78	84.4887	99.9056
84	84.7973	99.9489
90	85.0560	99.9723
96	85.2742	99.9850
102	85.4591	99.9919
108	85.6163	99.9956
114	85.7505	99.9976
120	85.8654	99.9987
126	85.9640	99.9993
132	86.0489	99.9996

Feed 9.8 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.5 l/h, equilibrated with 9.8 N HNO_3
Scrub 9.8 N HNO_3, 2.0 l/h

Table 6.6 The Effect of Number of Stages on Europium Purification, HNO_3 9.8 N, TBP 2.6 l/h.

STAGE	% RECOVERY	% PURITY
42	87.1070	93.2620
48	88.3687	95.8596
54	89.3841	97.4679
60	90.2185	98.4556
66	90.9161	99.0593
72	91.5079	99.4274
78	92.0161	99.6515
84	92.4573	99.7879
90	92.8438	99.8709
96	93.1851	99.9214
102	93.4886	99.9521
108	93.7603	99.9708
114	94.0048	99.9822
120	94.2260	99.9892
126	94.4271	99.9934
132	94.6106	99.9960

Feed 9.8 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.6 l/h, equilibrated with 9.8 N HNO_3
Scrub 9.8 N HNO_3, 2.0 l/h

Table 6.7 The Effect of Number of Stages on Europium Purification, HNO_3 9.9 N, TBP 2.2 l/h.

STAGE	% RECOVERY	% PURITY
42	69.3182	98.6852
48	69.9696	99.4156
54	70.4379	99.7405
60	70.7774	99.8847
66	71.0240	99.9488
72	71.2050	99.9772
78	71.3373	99.9899
84	71.4346	99.9955
90	71.5062	99.9980
96	71.5590	99.9991
102	71.5980	99.9996
108	71.6268	99.9998
114	71.6481	99.9999
120	71.6638	99.9999
126	71.6755	99.9999
132	71.6842	99.9999

Feed 9.9 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.2 l/h, equilibrated with 9.9 N HNO_3
Scrub 9.9 N HNO_3, 2.0 l/h

Table 6.8 The Effect of Number of Stages on Europium Purification, HNO_3 9.9 N, TBP 2.3 l/h.

STAGE	% RECOVERY	% PURITY
42	78.6484	97.3731
48	79.6610	98.6644
54	80.4461	99.3225
60	81.0641	99.6566
66	81.5567	99.8259
72	81.9536	99.9117
78	82.2760	99.9552
84	82.5397	99.9772
90	82.7567	99.9884
96	82.9361	99.9941
102	83.0850	99.9970
108	83.2089	99.9985
114	83.3125	99.9992
120	83.3992	99.9996
126	83.4720	99.9998
132	83.5330	99.9999

Feed 9.9 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.3 l/h, equilibrated with 9.9 N HNO_3
Scrub 9.9 N HNO_3, 2.0 l/h

Table 6.9 The Effect of Number of Stages on Europium Purification, HNO_3 9.9 N, TBP 2.4 l/h.

STAGE	% RECOVERY	% PURITY
42	86.1331	94.9434
48	87.3786	97.0659
54	88.3796	98.3045
60	89.2008	99.0222
66	89.8861	99.4366
72	90.4661	99.6754
78	90.9631	99.8130
84	91.3933	99.8922
90	91.7692	99.9379
96	92.1001	99.9642
102	92.3935	99.9793
108	92.6551	99.9881
114	92.8898	99.9931
120	93.1013	99.9960
126	93.2927	99.9977
132	93.4667	99.9987

Feed 9.9 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.4 l/h, equilibrated with 9.9 N HNO_3
Scrub 9.9 N HNO_3, 2.0 l/h

Table 6.10 The Effect of Number of Stages on Europium Purification, HNO_3 9.9 N, TBP 2.5 l/h.

STAGE	% RECOVERY	% PURITY
42	91.5676	90.7664
48	92.8117	93.9040
54	93.8024	95.9945
60	94.6074	97.3761
66	95.2724	98.2843
72	95.8294	98.8795
78	96.3012	99.2686
84	96.7048	99.5228
90	97.0529	99.6886
96	97.3554	99.7968
102	97.6199	99.8674
108	97.8523	99.9135
114	98.0577	99.9435
120	98.2398	99.9631
126	98.4020	99.9759
132	98.5469	99.9843

Feed 9.9 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.5 l/h, equilibrated with 9.9 N HNO_3
Scrub 9.9 N HNO_3, 2.0 l/h

Table 6.11 The Effect of Number of Stages on Europium Purification, HNO_3 10.0 N, TBP 2.1 l/h.

STAGE	% RECOVERY	% PURITY
42	75.0876	98.3907
48	75.9616	99.2526
54	76.6220	99.6532
60	77.1267	99.8391
66	77.5164	99.9253
72	77.8196	99.9653
78	78.0571	99.9839
84	78.2440	99.9925
90	78.3917	99.9965
96	78.5089	99.9984
102	78.6021	99.9992
108	78.6976	99.9995
114	78.7356	99.9998
120	78.7830	99.9999
126	78.8209	99.9999
132	78.8512	99.9999

Feed 10.0 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.1 l/h, equilibrated with 10.0 N HNO_3
Scrub 10.0 N HNO_3, 2.0 l/h

Table 6.12 The Effect of Number of Stages on Europium Purification, HNO_3 10.0 N, TBP 2.2 l/h.

STAGE	% RECOVERY	% PURITY
42	83.9143	96.6536
48	85.1071	98.2080
54	86.0594	99.0432
60	86.8346	99.4897
66	87.4759	99.7278
72	88.0135	99.8548
78	88.4694	99.9225
84	88.8597	99.9586
90	89.1967	99.9779
96	89.4896	99.9882
102	89.7458	99.9937
108	90.0402	99.9958
114	90.1703	99.9982
120	90.3470	99.9990
126	90.5044	99.9995
132	90.6452	99.9997

Feed 10.0 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.2 l/h, equilibrated with 10.0 N HNO_3
Scrub 10.0 N HNO_3, 2.0 l/h

Table 6.13 The Effect of Number of Stages on Europium Purification, HNO_3 10.0 N, TBP 2.3 l/h.

STAGE	% RECOVERY	% PURITY
42	90.3969	93.3760
48	91.6635	95.9195
54	92.6786	97.4977
60	93.5093	98.4693
66	94.2008	99.0649
72	94.7847	99.4291
78	95.2837	99.6515
84	95.7145	99.7873
90	96.0899	99.8701
96	96.4194	99.9207
102	96.7106	99.9516
108	97.0495	99.9652
114	97.2010	99.9819
120	97.4090	99.9889
126	97.5966	99.9932
132	97.7663	99.9959

Feed 10.0 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.3 l/h, equilibrated with 10.0 N HNO_3
Scrub 10.0 N HNO_3, 2.0 l/h

Table 6.14 The Effect of Number of Stages on Europium Purification, HNO_3 10.1 N, TBP 2.0 l/h.

STAGE	% RECOVERY	% PURITY
42	76.1591	98.5175
48	77.0755	99.3197
54	77.7738	99.6881
60	78.3127	99.8569
66	78.7331	99.9343
72	79.0639	99.9698
78	79.3260	99.9861
84	79.5349	99.9936
90	79.7021	99.9971
96	79.8365	99.9986
102	79.9448	99.9994
108	80.0323	99.9997
114	80.1031	99.9999
120	80.1606	99.9999
126	80.2073	99.9999
132	80.2452	99.9999

Feed 10.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.0 l/h, equilibrated with 10.1 N HNO_3
Scrub 10.1 N HNO_3, 2.0 l/h

Table 6.15 The Effect of Number of Stages on Europium Purification, HNO_3 10.1 N, TBP 2.1 l/h.

STAGE	% RECOVERY	% PURITY
42	85.1513	96.7813
48	86.3758	98.2850
54	87.3578	99.0887
60	88.1613	99.5163
66	88.8297	99.7432
72	89.3936	99.8636
78	89.8750	99.9276
84	90.2900	99.9615
90	90.6511	99.9795
96	90.9675	99.9891
102	91.2466	99.9942
108	91.4943	99.9969
114	91.7153	99.9984
120	91.9133	99.9991
126	92.0915	99.9995
132	92.2523	99.9998

Feed 10.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.1 l/h, equilibrated with 10.1 N HNO_3
Scrub 10.1 N HNO_3, 2.0 l/h

Table 6.16 The Effect of Number of Stages on Europium Purification, HNO_3 10.1 N, TBP 2.2 l/h.

STAGE	% RECOVERY	% PURITY
42	91.5144	93.3810
48	92.7591	95.9144
54	93.7508	97.4893
60	94.5570	98.4609
66	95.2234	99.0578
72	95.7819	99.4235
78	96.2553	99.6474
84	96.6605	99.7843
90	97.0103	99.8680
96	97.3144	99.9192
102	97.5805	99.9506
108	97.8145	99.9697
114	98.0214	99.9815
120	98.2050	99.9887
126	98.3686	99.9930
132	98.5149	99.9957

Feed 10.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.2 l/h, equilibrated with 10.1 N HNO_3
Scrub 10.1 N HNO_3, 2.0 l/h

Table 6.17 The Effect of Number of Stages on Europium Purification, HNO_3 10.2 N, TBP 1.9 l/h.

STAGE	% RECOVERY	% PURITY
42	80.3717	98.3238
48	81.4497	99.2093
54	82.2953	99.6274
60	82.9698	99.8244
66	83.5154	99.9171
72	83.9618	99.9609
78	84.3305	99.9815
84	84.6375	99.9913
90	84.8947	99.9959
96	85.1114	99.9980
102	85.2949	99.9991
108	85.4509	99.9996
114	85.5839	99.9998
120	85.6977	99.9999
126	85.7953	99.9999
132	85.8792	99.9999

Feed 10.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 1.9 l/h, equilibrated with 10.2 N HNO_3
Scrub 10.2 N HNO_3, 2.0 l/h

Table 6.18 The Effect of Number of Stages on Europium Purification, HNO_3 10.2 N, TBP 2.0 l/h.

STAGE	% RECOVERY	% PURITY
42	88.7225	96.1836
48	89.9968	97.8896
54	91.0229	98.8367
60	91.8666	99.3596
66	92.5725	99.6475
72	93.1717	99.8060
78	93.6868	99.8932
84	94.1342	99.9412
90	94.5265	99.9678
96	94.8732	99.9821
102	95.1818	99.9901
108	95.4582	99.9946
114	95.7073	99.9970
120	95.9328	99.9983
126	96.1379	99.9991
132	96.3254	99.9995

Feed 10.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.0 l/h, equilibrated with 10.2 N HNO_3
Scrub 10.2 N HNO_3, 2.0 l/h

Table 6.19 The Effect of Number of Stages on Europium Purification, HNO_3 10.2 N, TBP 2.1 l/h.

STAGE	% RECOVERY	% PURITY
42	94.0916	91.8975
48	95.2189	94.7645
54	96.0918	96.6322
60	96.7799	97.8397
66	97.3300	98.6166
72	97.7748	99.1150
78	98.1378	99.4341
84	98.4362	99.6382
90	98.6831	99.7687
96	98.8883	99.8522
102	99.0597	99.9055
108	99.2034	99.9396
114	99.3242	99.9614
120	99.4259	99.9753
126	99.5119	99.9842
132	99.5846	99.9899

Feed 10.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 100.0 g/l
Solvent TBP 2.1 l/h, equilibrated with 10.2 N HNO_3
Scrub 10.2 N HNO_3, 2.0 l/h

Table 7.2 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.1 N, TBP 3.1 l/h.

STAGE	% RECOVERY	% PURITY
18	92.7533	98.6399
24	95.7077	98.9812
30	97.3829	99.2020
36	98.3793	99.3547
42	98.9883	99.4662
48	99.3660	99.5510
54	99.6020	99.6175
60	99.7750	99.6710
66	99.8430	99.7147
72	99.9014	99.7510
78	99.9381	99.7816
84	99.9612	99.8075
90	99.9756	99.8298
96	99.9847	99.8490
102	99.9904	99.8656
108	99.9940	99.8802
114	99.9962	99.8929
120	99.9976	99.9041
126	99.9985	99.9140
132	99.9991	99.9228
138	99.9994	99.9305
144	99.9996	99.9375

Feed 6.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.1 l/h, equilibrated with 6.1 N HNO_3
Scrub 6.1 N HNO_3, 2.0 l/h

Table 7.3 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.1 N, TBP 3.2 l/h.

STAGE	% RECOVERY	% PURITY
18	91.0069	98.8651
24	94.2481	99.2040
30	96.1913	99.4183
36	97.4288	99.5610
42	98.2439	99.6615
48	98.7926	99.7351
54	99.1669	99.7903
60	99.4242	99.8326
66	99.6018	99.8655
72	99.7246	99.8914
78	99.8096	99.9119
84	99.8685	99.9278
90	99.9091	99.9416
96	99.9372	99.9523
102	99.9567	99.9610
108	99.9701	99.9680
114	99.9794	99.9738
120	99.9858	99.9785
126	99.9902	99.9823
132	99.9932	99.9855
138	99.9953	99.9881
144	99.9968	99.9902

Feed 6.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.2 l/h, equilibrated with 6.1 N HNO_3
Scrub 6.1 N HNO_3, 2.0 l/h

Table 7.4 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.1 N, TBP 3.3 l/h.

STAGE	% RECOVERY	% PURITY
18	89.0062	99.0524
24	92.4506	99.3813
30	94.6152	99.5796
36	96.0702	99.7046
42	97.0830	99.7899
48	97.8140	99.8481
54	98.3511	99.8892
60	98.7511	99.9187
66	99.0519	99.9400
72	99.2794	99.9556
78	99.4521	99.9670
84	99.5836	99.9753
90	99.6833	99.9817
96	99.7594	99.9864
102	99.8173	99.9898
108	99.8615	99.9923
114	99.8949	99.9943
120	99.9203	99.9958
126	99.9396	99.9968
132	99.9543	99.9976
138	99.9654	99.9982
144	99.9738	99.9987

Feed 6.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.3 l/h, equilibrated with 6.1 N HNO_3
Scrub 6.1 N HNO_3, 2.0 l/h

Table 7.5 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.1 N, TBP 3.4 l/h.

STAGE	% RECOVERY	% PURITY
18	86.7247	99.2110
24	90.2918	99.5203
30	92.6018	99.6977
36	94.2084	99.8043
42	95.3774	99.8713
48	96.2587	99.9144
54	96.9412	99.9427
60	97.4808	99.9616
66	97.9140	99.9740
72	98.2660	99.9824
78	98.5548	99.9881
84	98.7940	99.9919
90	98.9913	99.9945
96	99.1563	99.9963
102	99.2942	99.9975
108	99.4097	99.9983
114	99.5064	99.9988
120	99.5876	99.9992
126	99.6556	99.9995
132	99.7126	99.9996
138	99.7604	99.9997
144	99.8003	99.9998

Feed 6.1 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.4 l/h, equilibrated with 6.1 N HNO_3
Scrub 6.1 N HNO_3, 2.0 l/h

Table 7.6 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.0 l/h.

STAGE	% RECOVERY	% PURITY
18	90.9953	98.8655
24	94.2361	99.2060
30	96.1850	99.4191
36	97.4242	99.5617
42	98.2405	99.6622
48	98.7902	99.7357
54	99.1651	99.7909
60	99.4229	99.8331
66	99.6608	99.8660
72	99.7239	99.8918
78	99.8091	99.9123
84	99.8680	99.9287
90	99.9088	99.9419
96	99.9370	99.9526
102	99.9565	99.9612
108	99.9700	99.9683
114	99.9793	99.9740
120	99.9857	99.9787
126	99.9901	99.9825
132	99.9932	99.9856
138	99.9953	99.9882
144	99.9968	99.9903

Feed 6.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.0 l/h, equilibrated with 6.2 N HNO_3
Scrub 6.2 N HNO_3, 2.0 l/h

Table 7.7 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.1 l/h.

STAGE	% RECOVERY	% PURITY
18	88.8417	99.0654
24	92.3015	99.3934
30	94.4857	99.5892
36	95.9528	99.7139
42	96.9817	99.7970
48	97.9255	99.8542
54	98.2743	99.8943
60	98.6852	99.9229
66	98.9957	99.9435
72	99.2318	99.9584
78	99.4121	99.9693
84	99.5501	99.9773
90	99.6558	99.9832
96	99.7368	99.9876
102	99.7989	99.9908
108	99.8464	99.9932
114	99.8827	99.9949
120	99.9105	99.9962
126	99.9318	99.9972
132	99.9480	99.9979
138	99.9604	99.9985
144	99.9698	99.9988

Feed 6.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.1 l/h, equilibrated with 6.2 N HNO_3
Scrub 6.2 N HNO_3, 2.0 l/h

Table 7.8 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.2 l/h.

STAGE	% RECOVERY	% PURITY
18	86.3826	99.2300
24	89.9535	99.5376
30	92.2849	99.7117
36	93.9080	99.8151
42	95.0934	99.8797
48	95.9910	99.9210
54	96.6897	99.9478
60	97.2451	99.9653
66	97.6940	99.9769
72	98.0614	99.9846
78	98.3652	99.9897
84	98.6183	99.9931
90	98.8305	99.9954
96	99.0093	99.9969
102	99.1603	99.9979
108	99.2883	99.9986
114	99.3968	99.9991
120	99.4891	99.9994
126	99.5674	99.9996
132	99.6340	99.9997
138	99.6906	99.9998
144	99.7386	99.9999

Feed 6.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.2 l/h, equilibrated with 6.2 N HNO_3
Scrub 6.2 N HNO_3, 2.0 l/h

Table 7.9 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.3 l/h.

STAGE	% RECOVERY	% PURITY
18	83.6241	99.3646
24	87.1825	99.6472
30	89.5498	99.7970
36	91.2243	99.8806
42	92.4663	99.9289
48	93.4222	99.9573
54	94.1800	99.9743
60	94.7951	99.9844
66	95.3041	99.9906
72	95.7322	99.9943
78	96.0971	99.9965
84	96.4117	99.9979
90	96.6856	99.9987
96	96.9262	99.9992
102	97.1391	99.9995
108	97.3288	99.9997
114	97.4988	99.9998
120	97.6519	99.9999
126	97.7905	99.9999
132	97.9165	99.9999
138	98.0315	99.9999
144	98.1368	99.9999

Feed 6.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.3 l/h, equilibrated with 6.2 N HNO_3
Scrub 6.2 N HNO_3, 2.0 l/h

Table 7.10 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.2 N, TBP 3.4 l/h.

STAGE	% RECOVERY	% PURITY
18	80.5822	99.4739
24	83.9992	99.7298
30	86.2835	99.8567
36	87.8952	99.9226
42	89.0799	99.9577
48	89.9789	99.9767
54	90.6786	99.9872
60	91.2339	99.9929
66	91.6815	99.9961
72	92.0466	99.9978
78	92.3471	99.9988
84	92.5964	99.9993
90	92.8043	99.9996
96	92.9784	99.9998
102	93.1246	99.9999
108	93.2476	99.9999
114	93.3514	99.9999
120	93.4382	99.9999
126	93.5214	99.9999
132	93.6002	99.9999
138	93.6687	99.9999
144	93.7029	99.9999

Feed 6.2 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.4 l/h, equilibrated with 6.2 N HNO_3
Scrub 6.2 N HNO_3, 2.0 l/h

Table 7.11 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.3 N, TBP 2.8 l/h.

STAGE	% RECOVERY	% PURITY
18	90.0098	98.9582
24	93.3693	99.2954
30	95.4408	99.5021
36	96.7954	99.6376
42	97.7168	99.7309
48	98.3597	99.7973
54	98.8158	99.8457
60	99.1428	99.8817
66	99.3787	99.9088
72	99.5495	99.9294
78	99.6733	99.9451
84	99.7632	99.9572
90	99.8285	99.9666
96	99.8758	99.9739
102	99.9101	99.9796
108	99.9350	99.9840
114	99.9530	99.9875
120	99.9660	99.9902
126	99.9754	99.9923
132	99.9822	99.9939
138	99.9872	99.9952
144	99.9907	99.9963

Feed 6.3 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.8 l/h, equilibrated with 6.3 N HNO_3
Scrub 6.3 N HNO_3, 2.0 l/h

Table 7.12 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.3 N, TBP 2.9 l/h.

STAGE	% RECOVERY	% PURITY
18	87.4909	99.1561
24	91.0306	99.4750
30	93.3130	99.6597
36	94.8812	99.7735
42	96.0097	99.8467
48	96.8498	99.8951
54	97.4909	99.9276
60	97.9892	99.9498
66	98.3817	99.9651
72	98.6940	99.9756
78	98.9442	99.9830
84	99.1457	99.9881
90	99.3085	99.9916
96	99.4403	99.9941
102	99.5471	99.9959
108	99.6337	99.9971
114	99.7040	99.9980
120	99.7609	99.9986
126	99.8071	99.9990
132	99.8444	99.9993
138	99.8746	99.9995
144	99.8990	99.9996

Feed 6.3 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.9 l/h, equilibrated with 6.3 N HNO_3
Scrub 6.3 N HNO_3, 2.0 l/h

Table 7.13 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.3 N, TBP 3.0 l/h.

STAGE	% RECOVERY	% PURITY
18	84.6121	99.3156
24	88.1918	99.6089
30	90.5631	99.7681
36	92.2353	99.8593
42	93.4727	99.9135
48	94.4232	99.9463
54	95.1751	99.9665
60	95.7841	99.9790
66	96.2868	99.9868
72	96.7084	99.9917
78	97.0666	99.9948
84	97.3744	99.9967
90	97.6413	99.9979
96	97.8747	99.9987
102	98.0801	99.9992
108	98.2621	99.9995
114	98.4242	99.9997
120	98.5692	99.9998
126	98.6994	99.9999
132	98.8188	99.9999
138	98.9229	99.9999
144	99.0190	99.9999

Feed 6.3 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.0 l/h, equilibrated with 6.3 N HNO_3
Scrub 6.3 N HNO_3, 2.0 l/h

Table 7.14 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.3 N, TBP 3.1 l/h.

STAGE	% RECOVERY	% PURITY
18	81.3892	99.4430
24	84.8564	99.7078
30	87.1762	99.8414
36	88.8174	99.9123
42	90.0296	99.9509
48	90.9556	99.9724
54	91.6821	99.9844
60	92.2643	99.9911
66	92.7388	99.9950
72	93.1309	99.9971
78	93.4583	99.9984
84	93.7342	99.9991
90	93.9684	99.9995
96	94.1682	99.9997
102	94.3394	99.9998
108	94.4867	99.9999
114	94.6136	99.9999
120	94.7233	99.9999
126	94.8182	99.9999
132	94.9003	99.9999
138	94.9714	99.9999
144	95.0330	100.0000

Feed 6.3 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.1 l/h, equilibrated with 6.3 N HNO_3
Scrub 6.3 N HNO_3, 2.0 l/h

Table 7.15 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.3 N, TBP 3.2 l/h.

STAGE	% RECOVERY	% PURITY
18	77.8520	99.5444
24	81.0563	99.7801
30	83.1893	99.8907
36	84.6740	99.9448
42	85.7414	99.9718
48	86.5276	99.9855
54	87.1172	99.9925
60	87.5652	99.9961
66	87.9090	99.9980
72	88.1745	99.9990
78	88.3804	99.9995
84	88.5406	99.9997
90	88.6654	99.9999
96	88.7627	99.9999
102	88.8386	99.9999
108	88.8977	99.9999
114	88.9438	99.9999
120	88.9797	99.9999
126	89.0076	99.9999
132	89.0292	99.9999
138	89.0461	99.9999
144	89.0592	100.0000

Feed 6.3 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.2 l/h, equilibrated with 6.3 N HNO_3
Scrub 6.3 N HNO_3, 2.0 l/h

Table 7.16 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.5 l/h.

STAGE	% RECOVERY	% PURITY
18	92.6828	98.6307
24	95.6561	98.9744
30	97.3459	99.1965
36	98.3531	99.3501
42	98.9698	99.4622
48	99.3531	99.5474
54	99.5931	99.6143
60	99.7744	99.6679
66	99.8389	99.7119
72	99.8986	99.7484
78	99.9362	99.7779
84	99.9599	99.8052
90	99.9748	99.8276
96	99.9842	99.8469
102	99.9900	99.8637
108	99.9937	99.8783
114	99.9961	99.8912
120	99.9975	99.9025
126	99.9984	99.9125
132	99.9990	99.9213
138	99.9994	99.9292
144	99.9996	99.9362

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.5 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

Table 7.17 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.6 l/h.

STAGE	% RECOVERY	% PURITY
18	90.4623	98.9038
24	93.7774	99.2448
30	95.7936	99.4561
36	97.0981	99.5962
42	97.9727	99.6940
48	98.5732	99.7645
54	98.9916	99.8169
60	99.2858	99.8564
66	99.4937	99.8868
72	99.6410	99.9103
78	99.7455	99.9286
84	99.8197	99.9431
90	99.8723	99.9545
96	99.9096	99.9635
102	99.9360	99.9708
108	99.9547	99.9765
114	99.9680	99.9811
120	99.9774	99.9848
126	99.9840	99.9878
132	99.9887	99.9902
138	99.9920	99.9921
144	99.9944	99.9936

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.6 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

Table 7.18 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.7 l/h.

STAGE	% RECOVERY	% PURITY
18	87.8294	99.1243
24	91.3557	99.4478
30	93.6192	99.6370
36	95.1667	99.7549
42	96.2740	99.8315
48	97.0927	99.8828
54	97.7127	99.9179
60	98.1904	99.9421
66	98.5631	99.9590
72	98.8563	99.9709
78	99.0885	99.9793
84	99.2731	99.9852
90	99.4203	99.9895
96	99.5378	99.9925
102	99.6317	99.9946
108	99.7066	99.9962
114	99.7665	99.9973
120	99.8143	99.9980
126	99.8524	99.9986
132	99.8828	99.9990
138	99.9070	99.9993
144	99.9262	99.9995

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.7 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

Table 7.19 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.8 l/h.

STAGE	% RECOVERY	% PURITY
18	84.7835	99.2998
24	88.3669	99.5968
30	90.7388	99.7759
36	92.4104	99.8525
42	93.6464	99.9084
48	94.5951	99.9427
54	95.3450	99.9639
60	95.9517	99.9772
66	96.4520	99.9855
72	96.8709	99.9908
78	97.2264	99.9942
84	97.5312	99.9963
90	97.7950	99.9976
96	98.0251	99.9985
102	98.2278	99.9990
108	98.4058	99.9994
114	98.5643	99.9996
120	98.7055	99.9997
126	98.8319	99.9998
132	98.9454	99.9999
138	99.0748	99.9999
144	99.1395	99.9999

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.8 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

Table 7.20 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 2.9 l/h.

STAGE	% RECOVERY	% PURITY
18	81.3420	99.4380
24	84.8080	99.7045
30	87.1281	99.8393
36	88.7698	99.9109
42	89.9822	99.9500
48	90.9083	99.9718
54	91.6346	99.9840
60	92.2164	99.9909
66	92.6904	99.9948
72	93.0818	99.9970
78	93.4084	99.9983
84	93.6835	99.9990
90	93.9166	99.9994
96	94.1154	99.9997
102	94.2855	99.9998
108	94.4317	99.9999
114	94.5575	99.9999
120	94.6661	99.9999
126	94.7599	99.9999
132	94.8409	99.9999
138	94.9109	99.9999
144	94.9715	99.9999

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 2.9 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

Table 7.21 The Effect of Number of Stages on Yttrium Purification, HNO_3 6.4 N, TBP 3.0 l/h.

STAGE	% RECOVERY	% PURITY
18	77.5412	99.5463
24	80.7175	99.7818
30	82.8308	99.8920
36	84.2991	99.9456
42	85.3516	99.9723
48	86.1238	99.9858
54	86.7000	99.9927
60	87.1355	99.9963
66	87.4674	99.9981
72	87.7722	99.9990
78	87.9180	99.9995
84	88.0692	99.9997
90	88.1861	99.9998
96	88.2765	99.9999
102	88.3463	99.9999
108	88.4002	99.9999
114	88.4419	99.9999
120	88.4740	99.9999
126	88.4988	99.9999
132	88.5179	99.9999
138	88.5326	99.9999
144	88.5439	100.0000

Feed 6.4 N HNO_3 1.0 l/h, center feed
Rare Earth in feed 10.0 g/l
Solvent TBP 3.0 l/h, equilibrated with 6.4 N HNO_3
Scrub 6.4 N HNO_3, 2.0 l/h

APPENDIX B

Figures

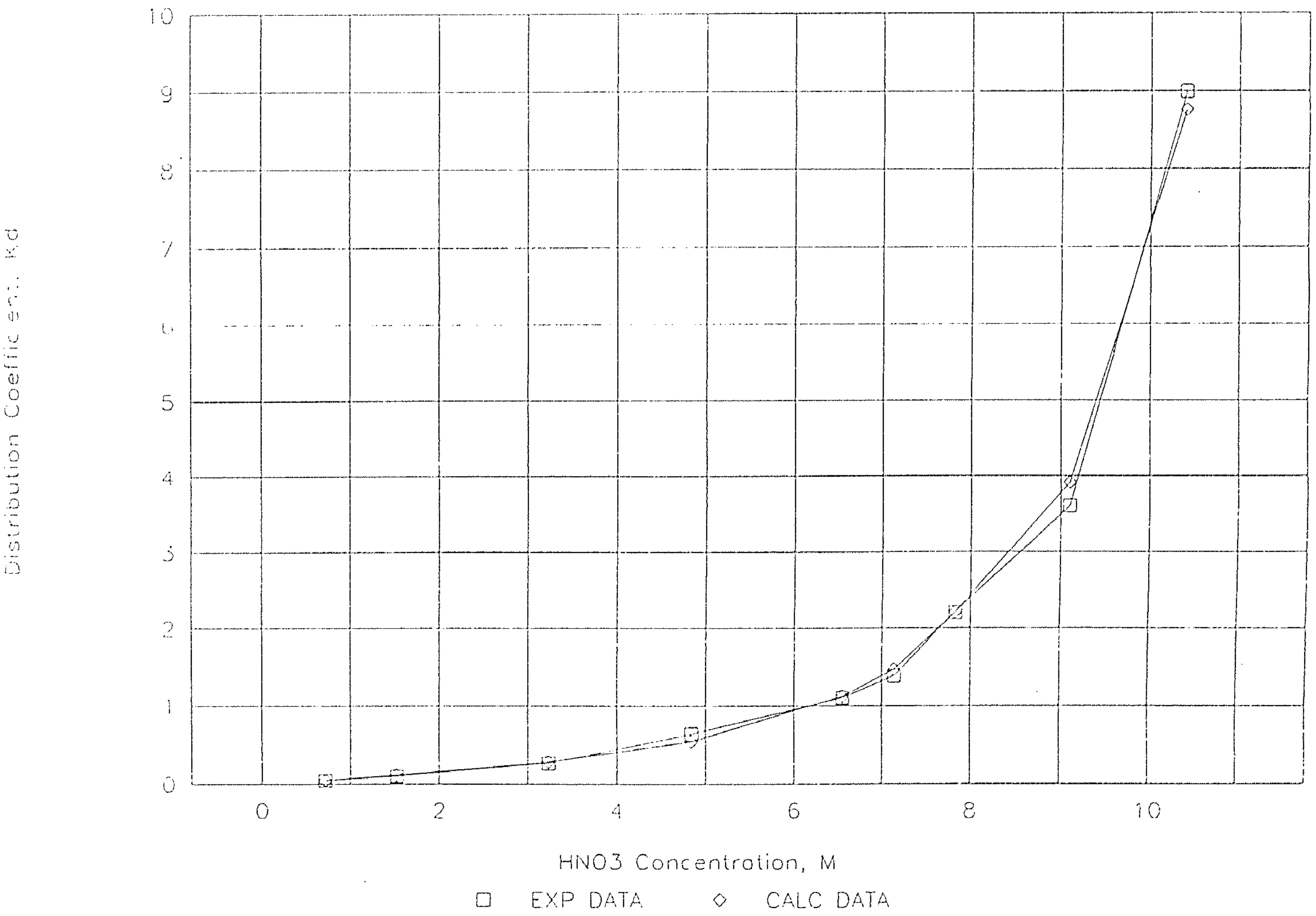

Figure 5.2 Comparison of the Experimental and Predicted Distribution Coefficients of Yttrium.

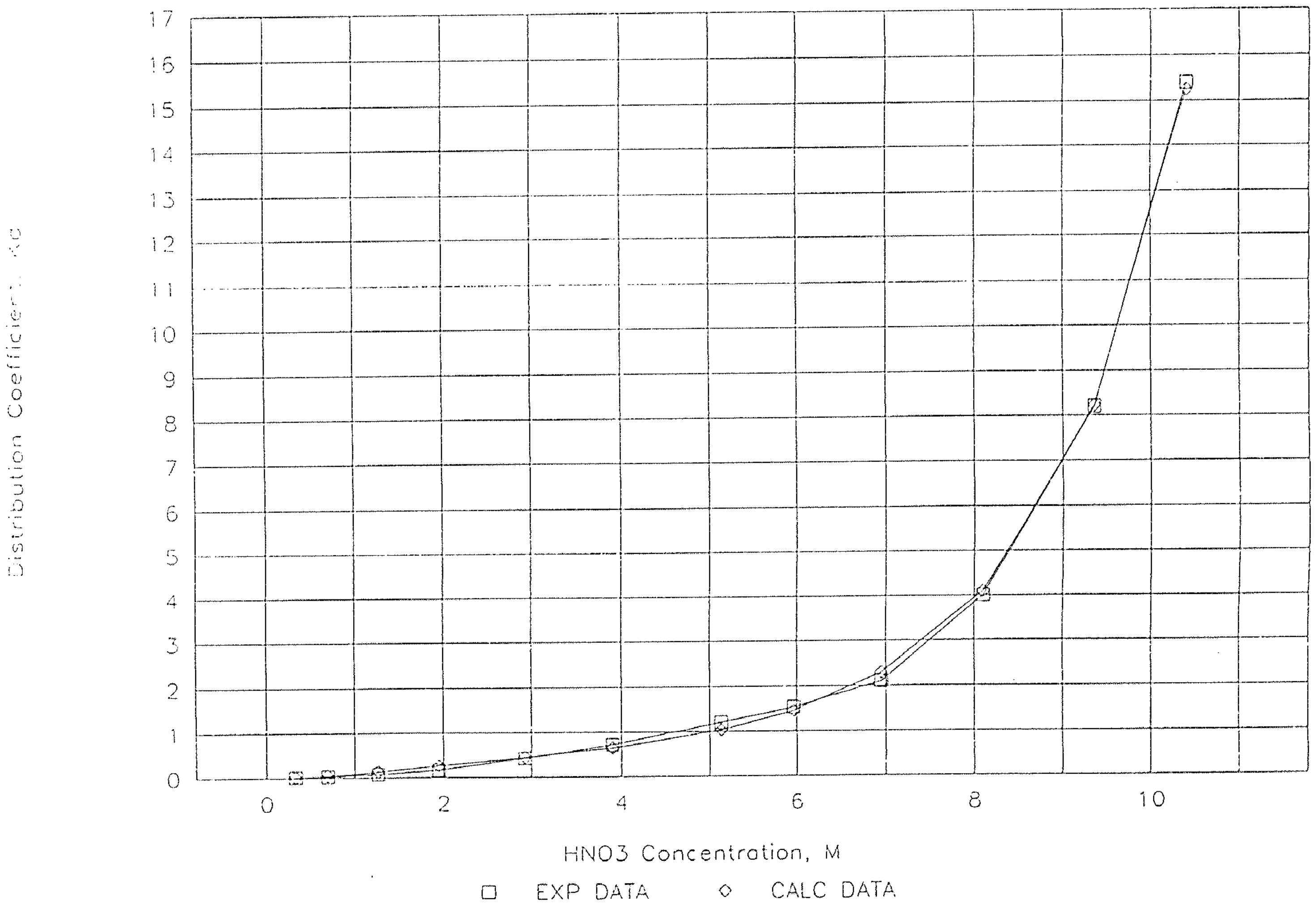

Figure 5.3 Comparison of the Experimental and Predicted Distribution Coefficients of Ytterbium.

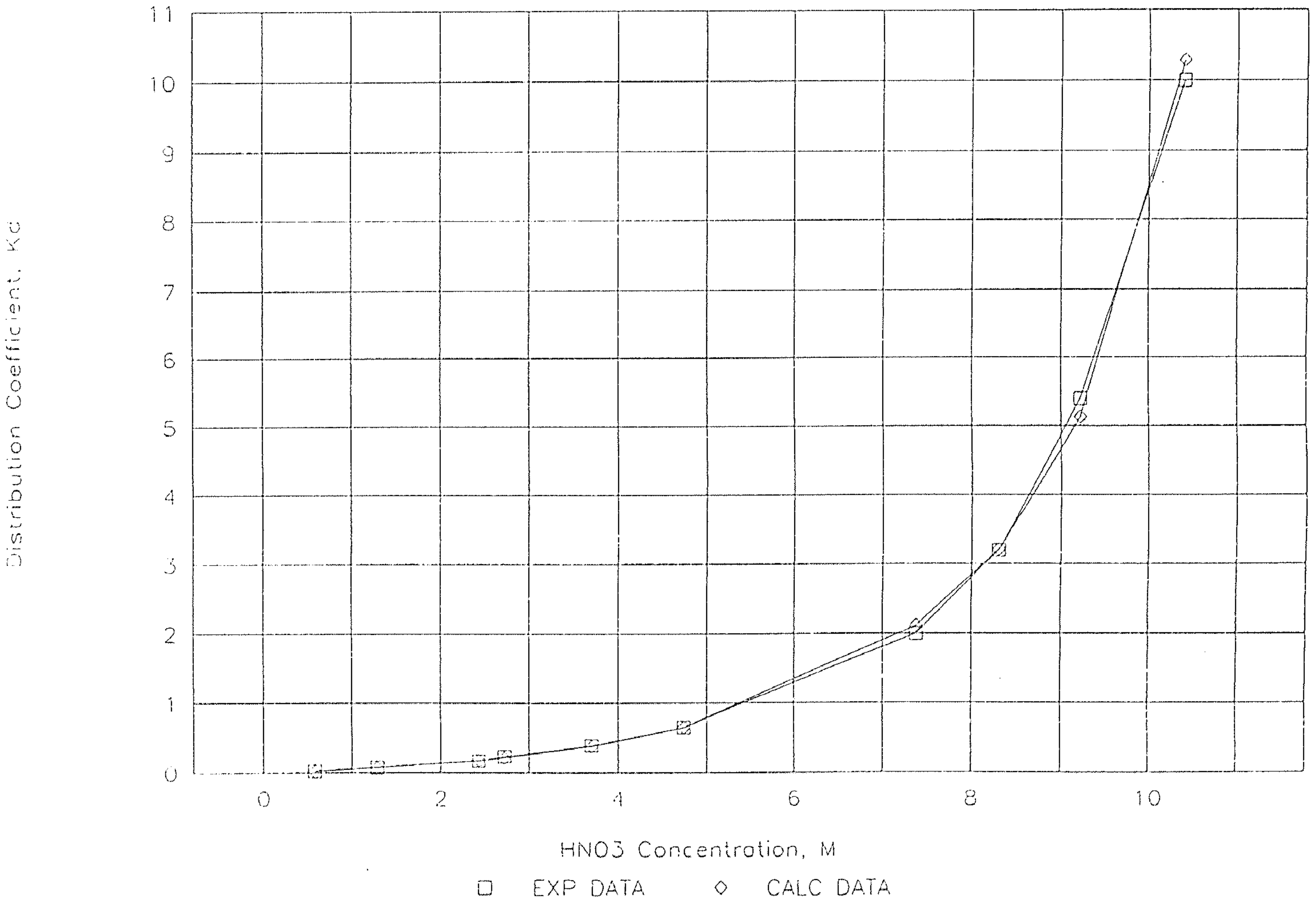

Figure 5.4 Comparison of the Experimental and Predicted Distribution Coefficients of Thulium.

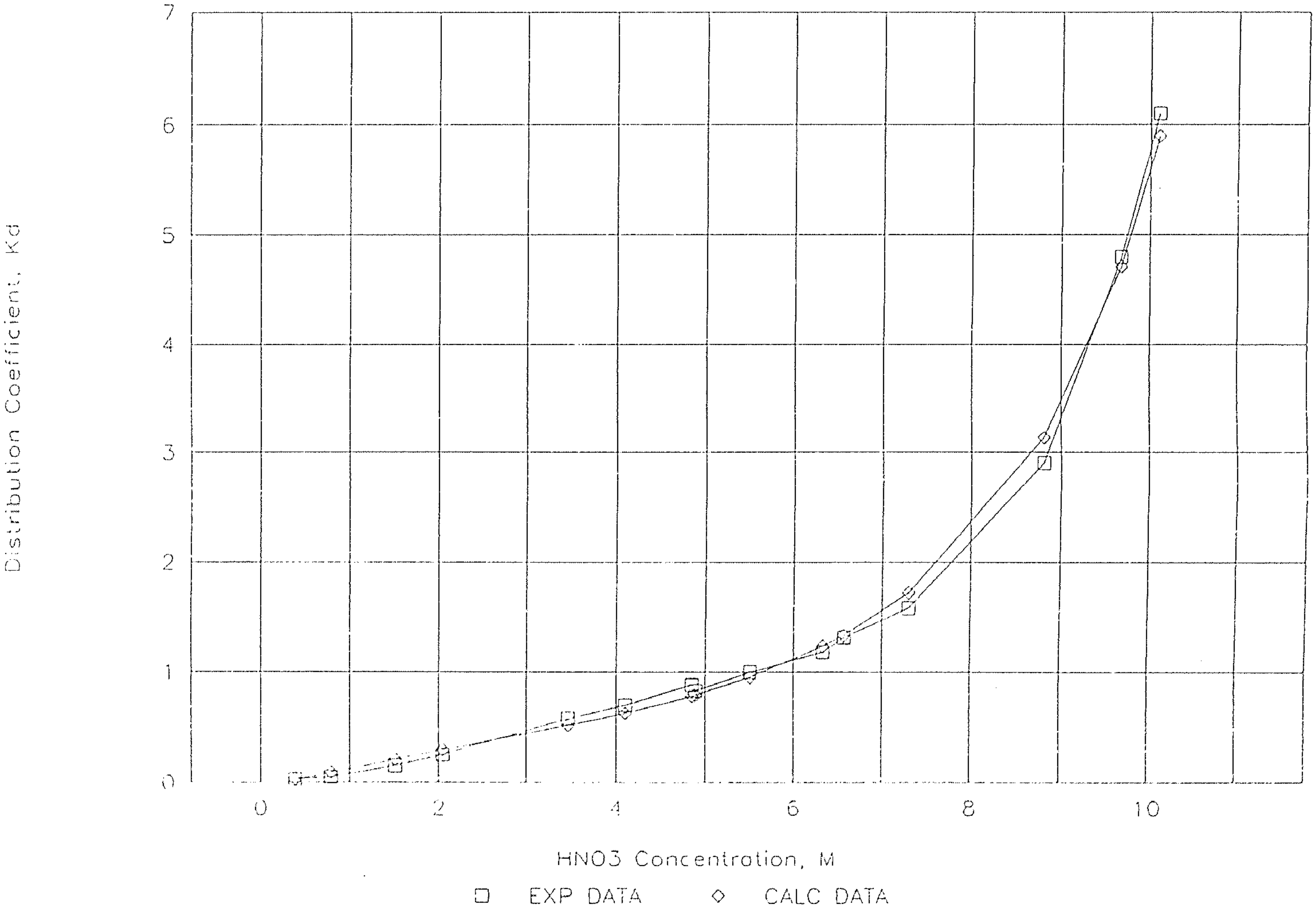

Figure 5.5 Comparison of the Experimental and Predicted Distribution Coefficients of Erbium.

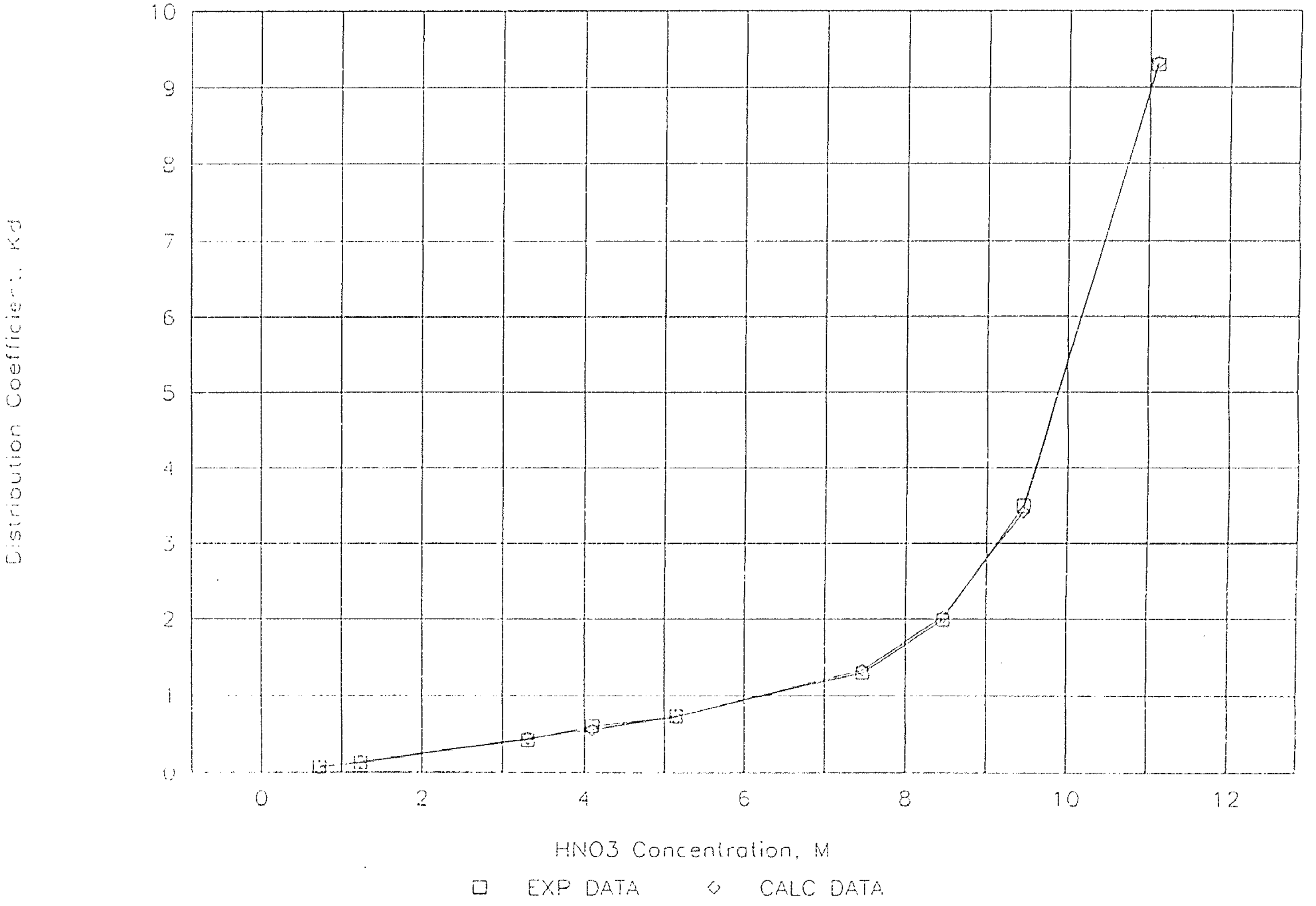

Figure 5.6 Comparison of the Experimental and Predicted Distribution Coefficients of Holmium.

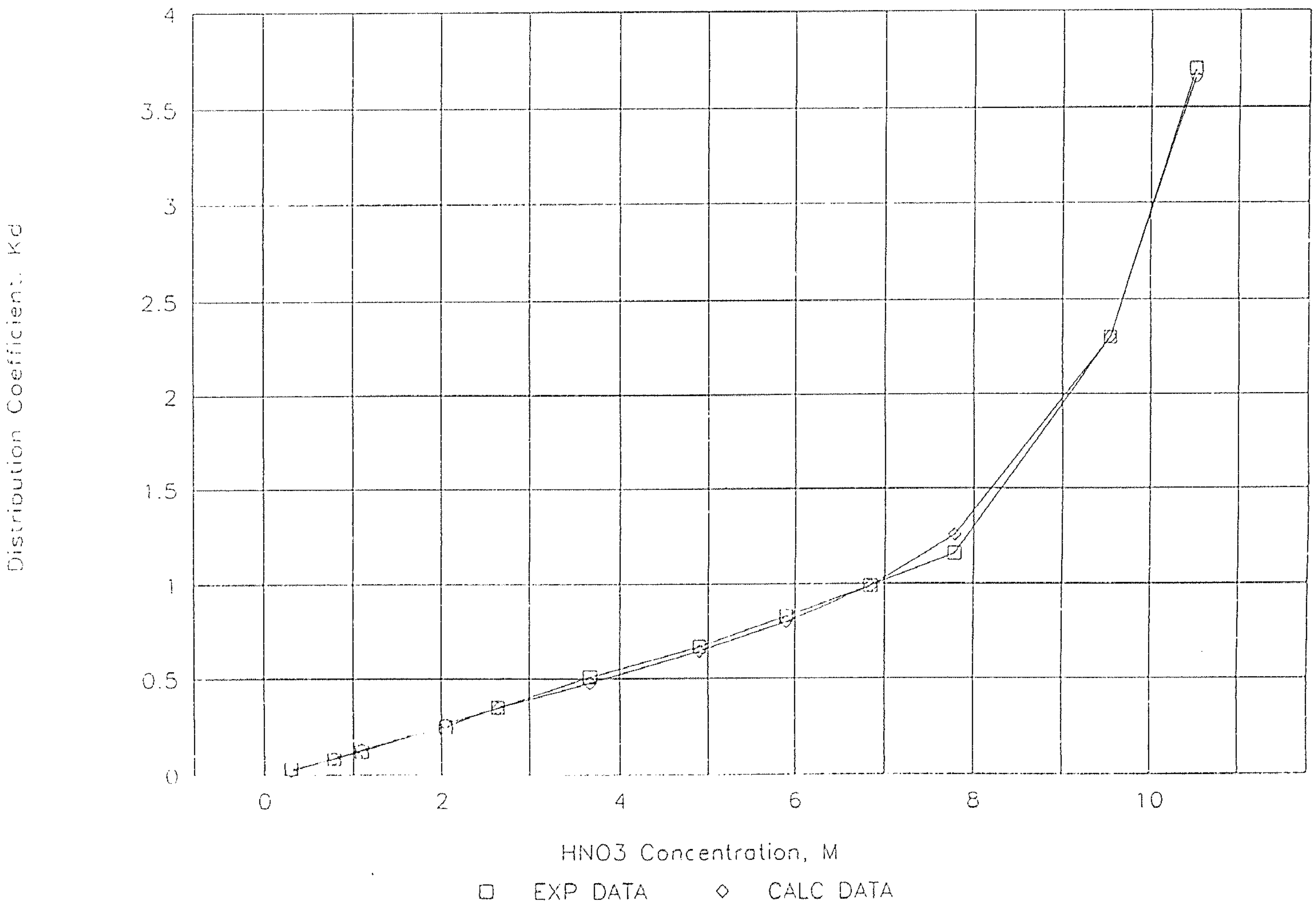

Figure 5.7 Comparison of the Experimental and Predicted Distribution Coefficients of Dysprosium.

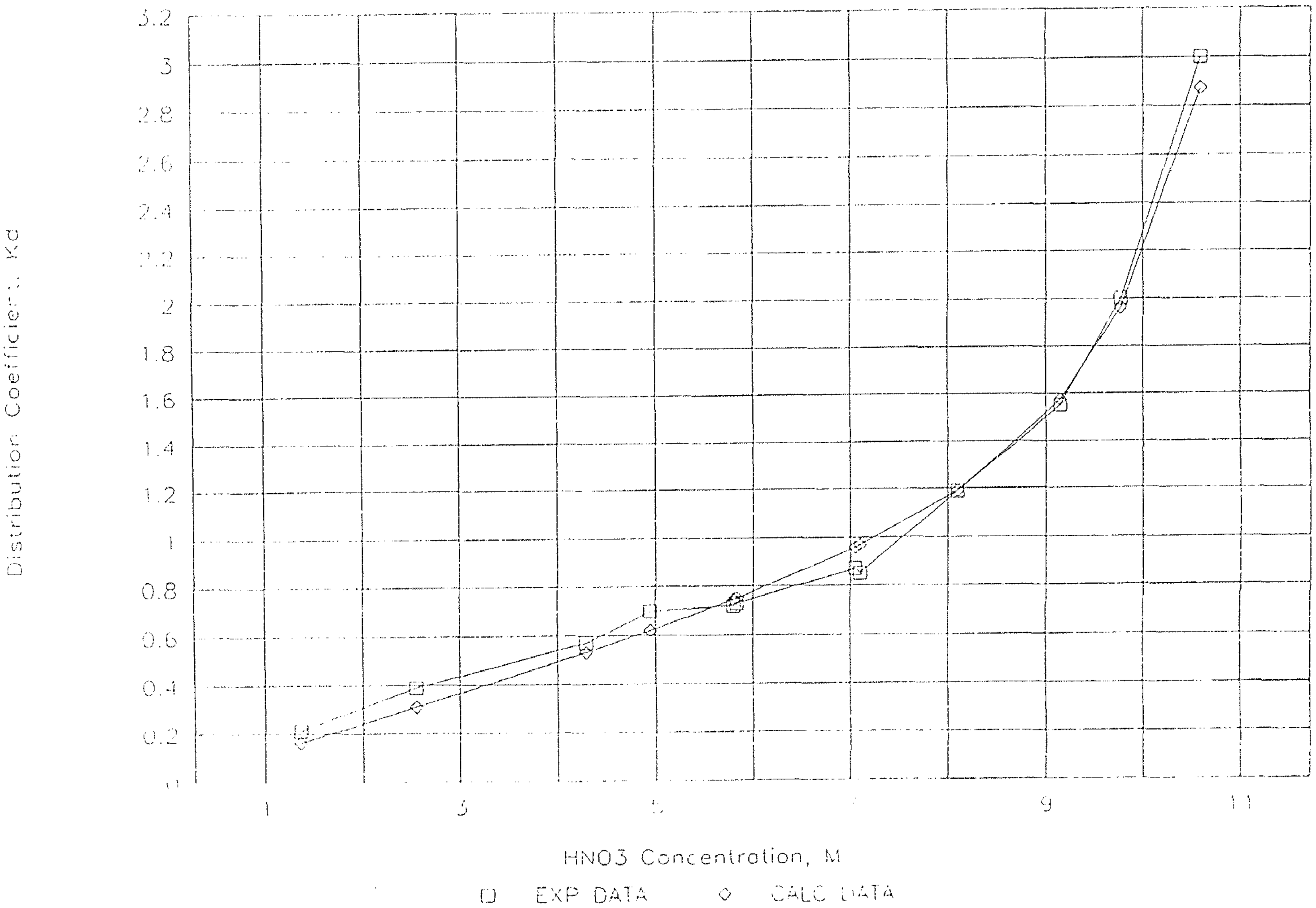

Figure 5.8 Comparison of the Experimental and Predicted Distribution Coefficients of Terbium.

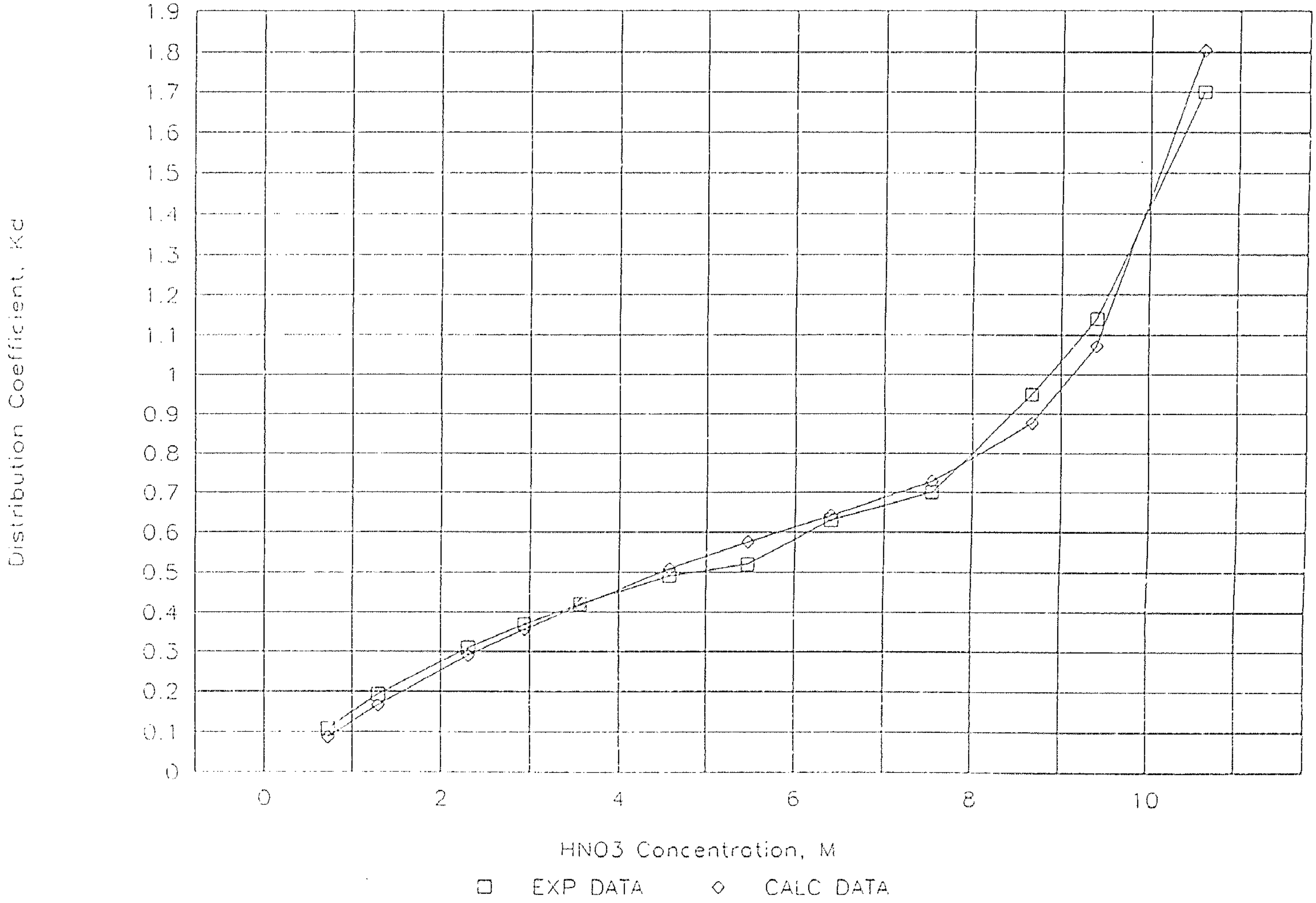

Figure 5.9 Comparison of the Experimental and Predicted Distribution Coefficients of Gadolinium.

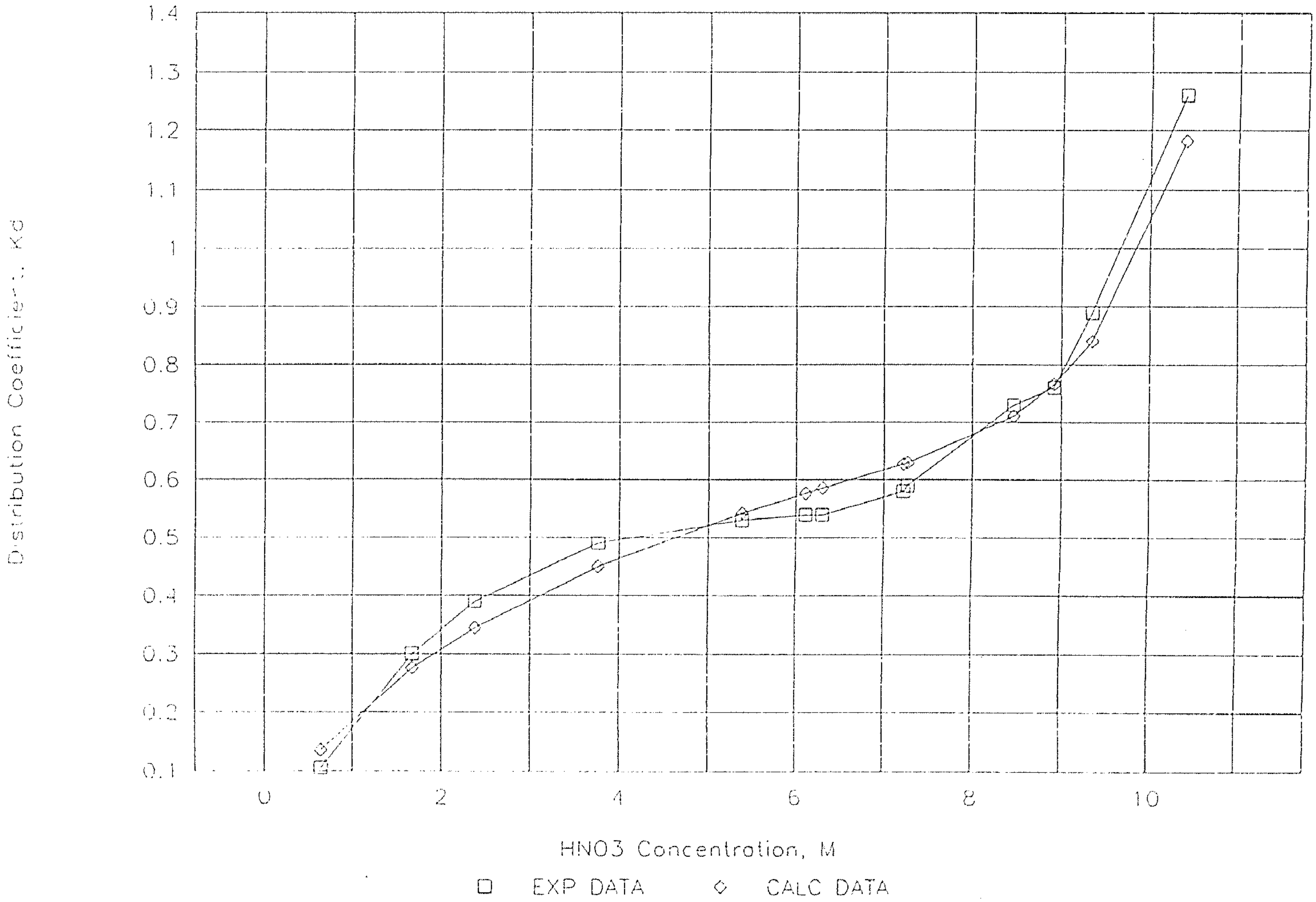

Figure 5.10 Comparison of the Experimental and Predicted Distribution Coefficients of Europium.

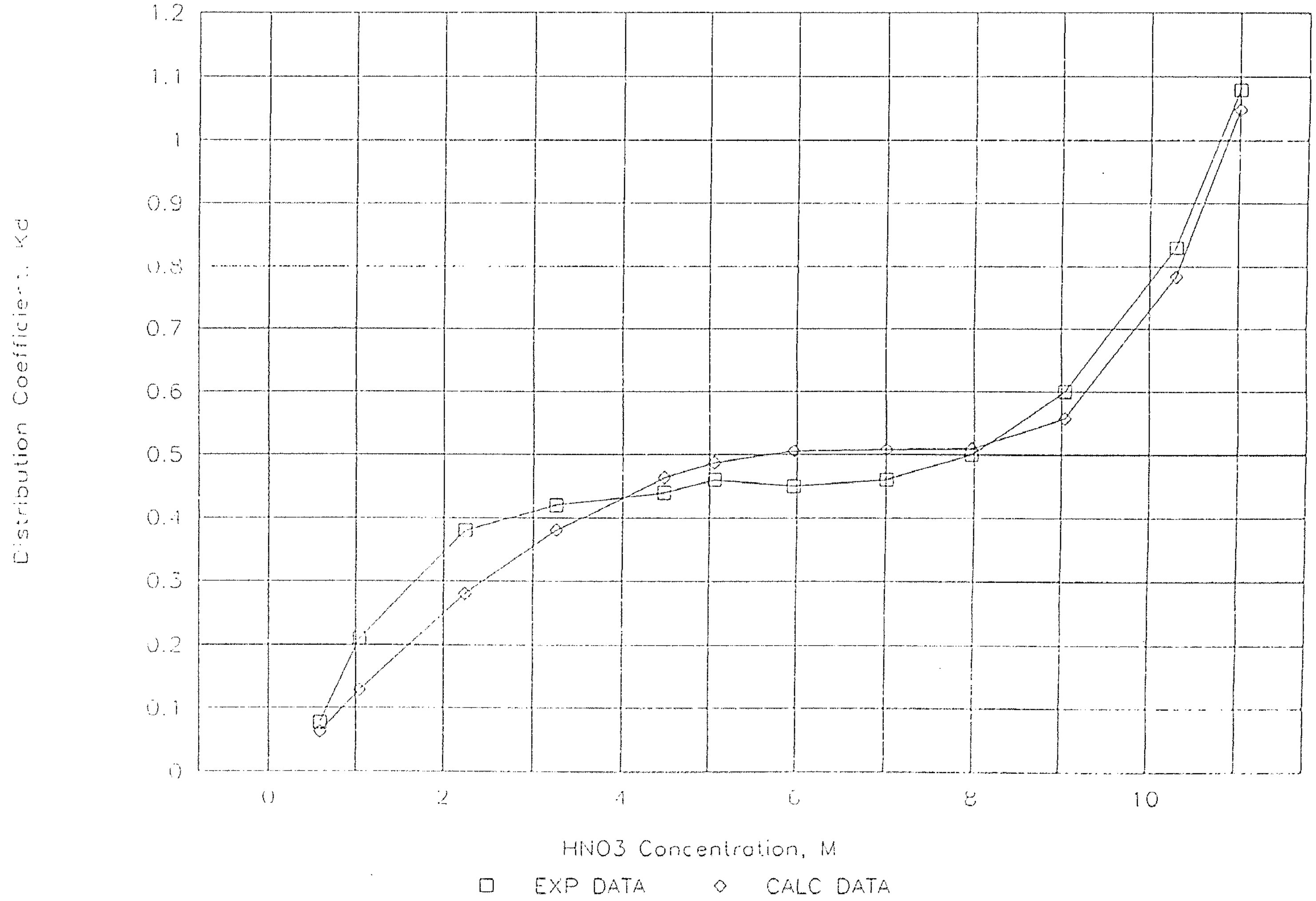

Figure 5.11 Comparison of the Experimental and Predicted Distribution Coefficients of Samarium.

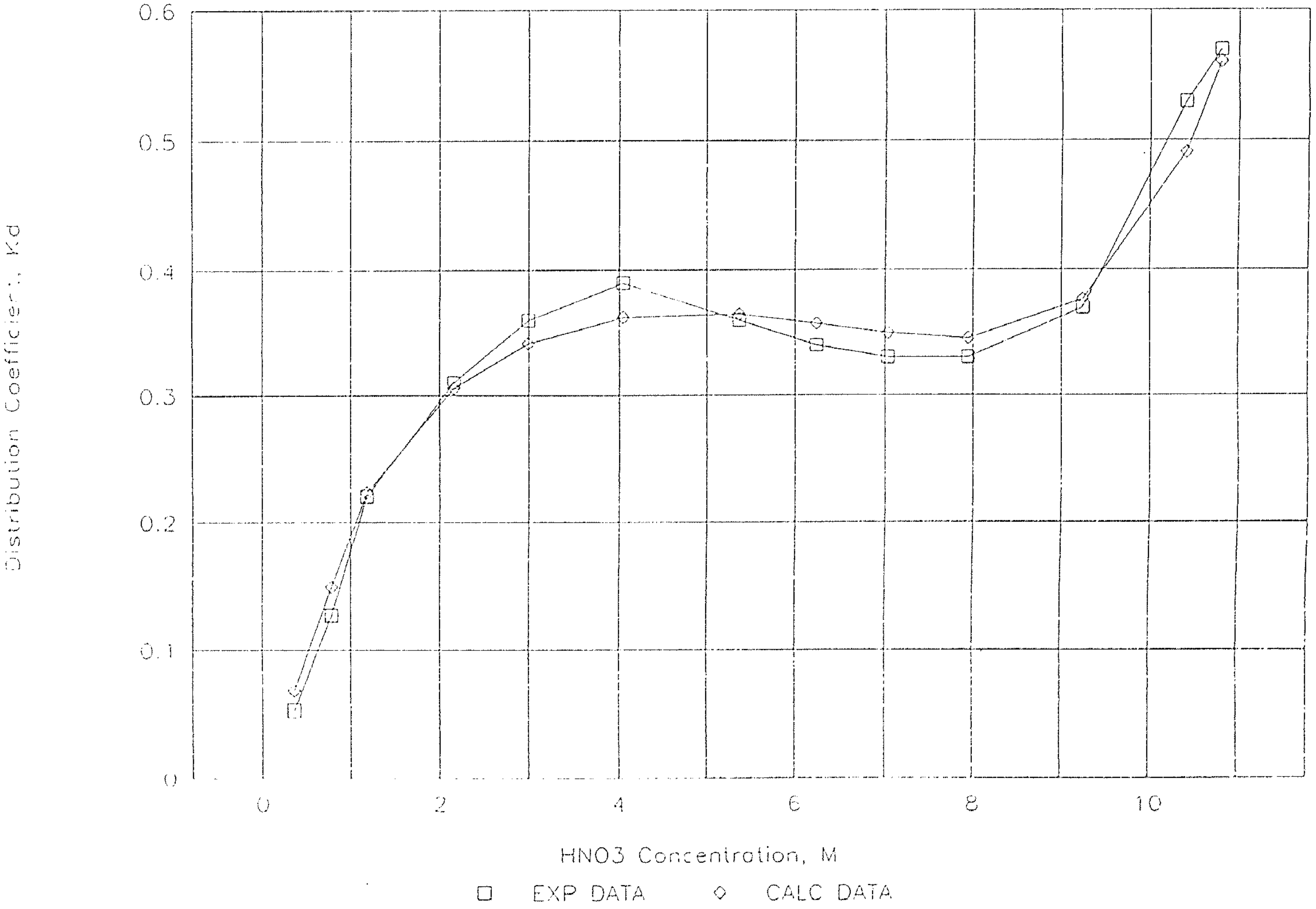

Figure 5.12 Comparison of the Experimental and Predicted Distribution Coefficients of Promethium.

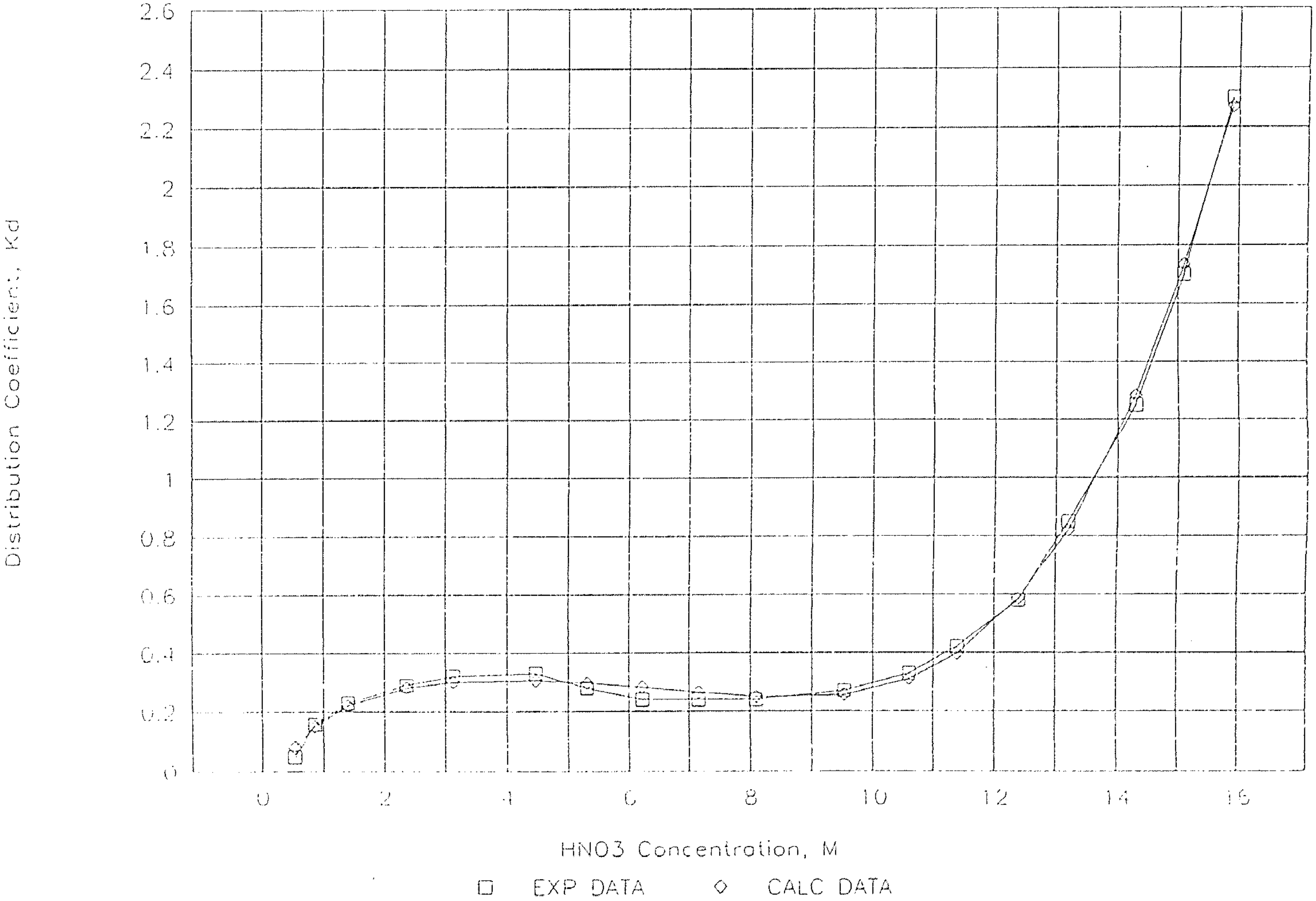

Figure 5.13 Comparison of the Experimental and Predicted Distribution Coefficients of Neodymium.

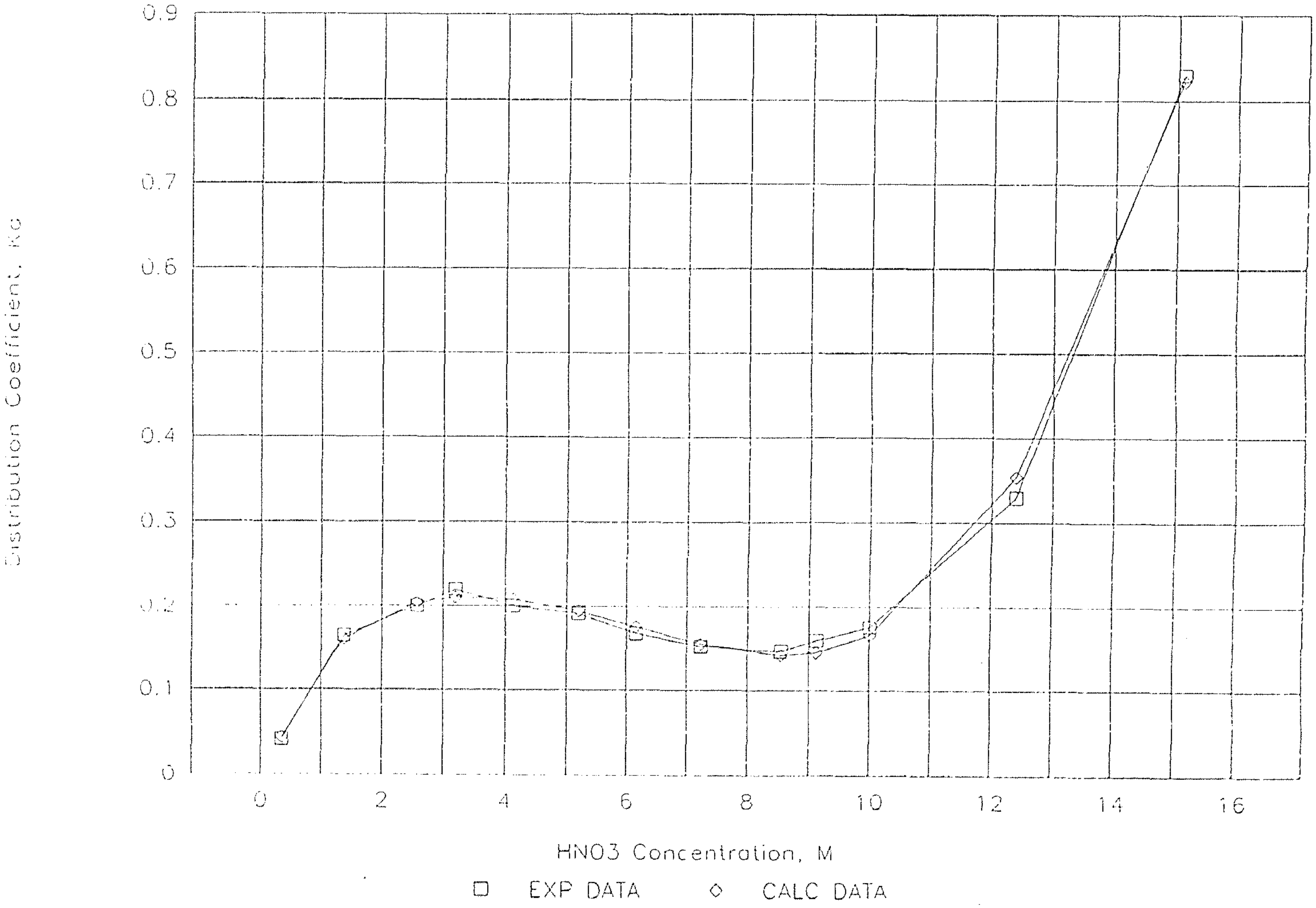

Figure 5.14 Comparison of the Experimental and Predicted Distribution Coefficients of Praseodymium.

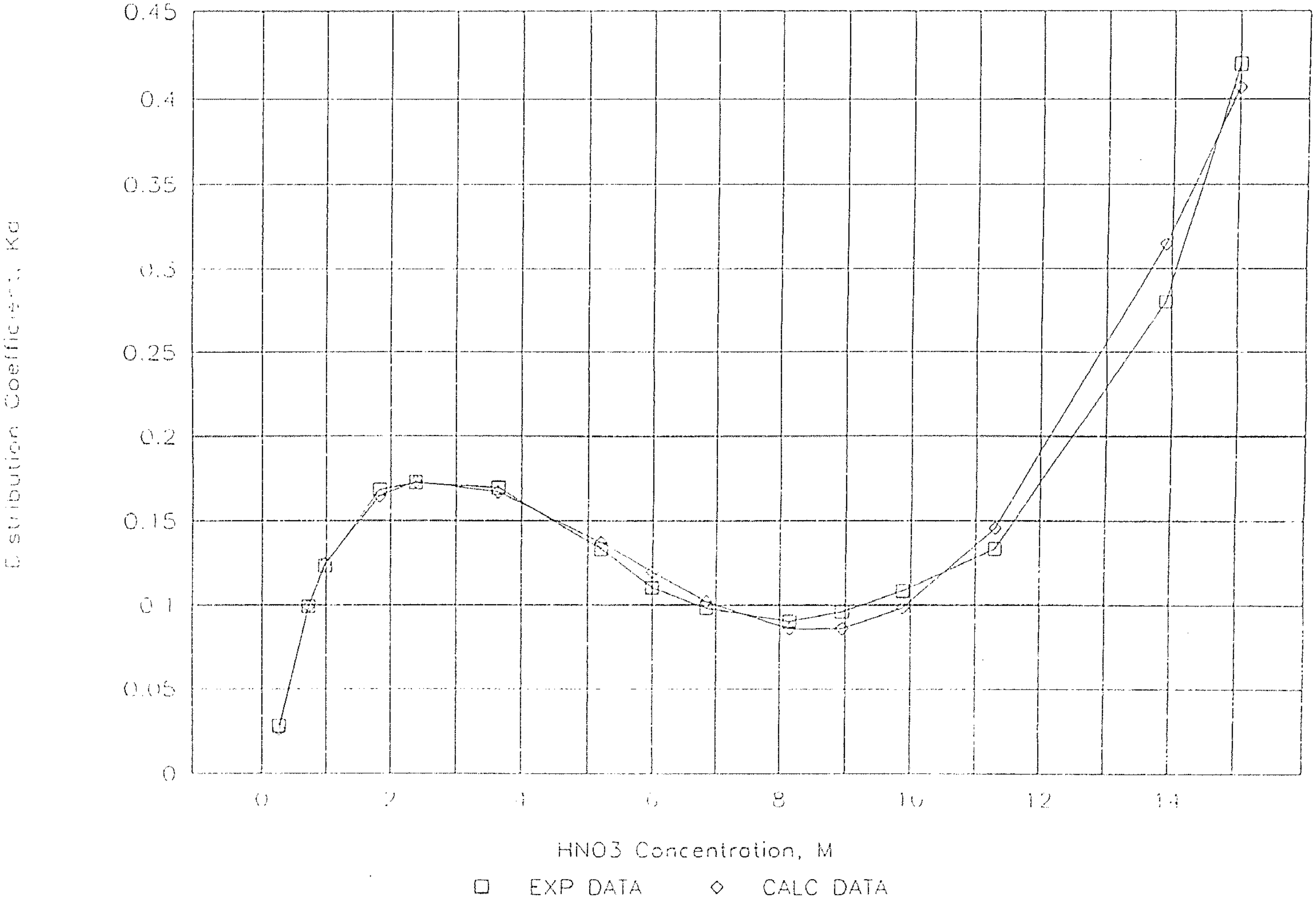

Figure 5.15 Comparison of the Experimental and Predicted Distribution Coefficients of Cerium.

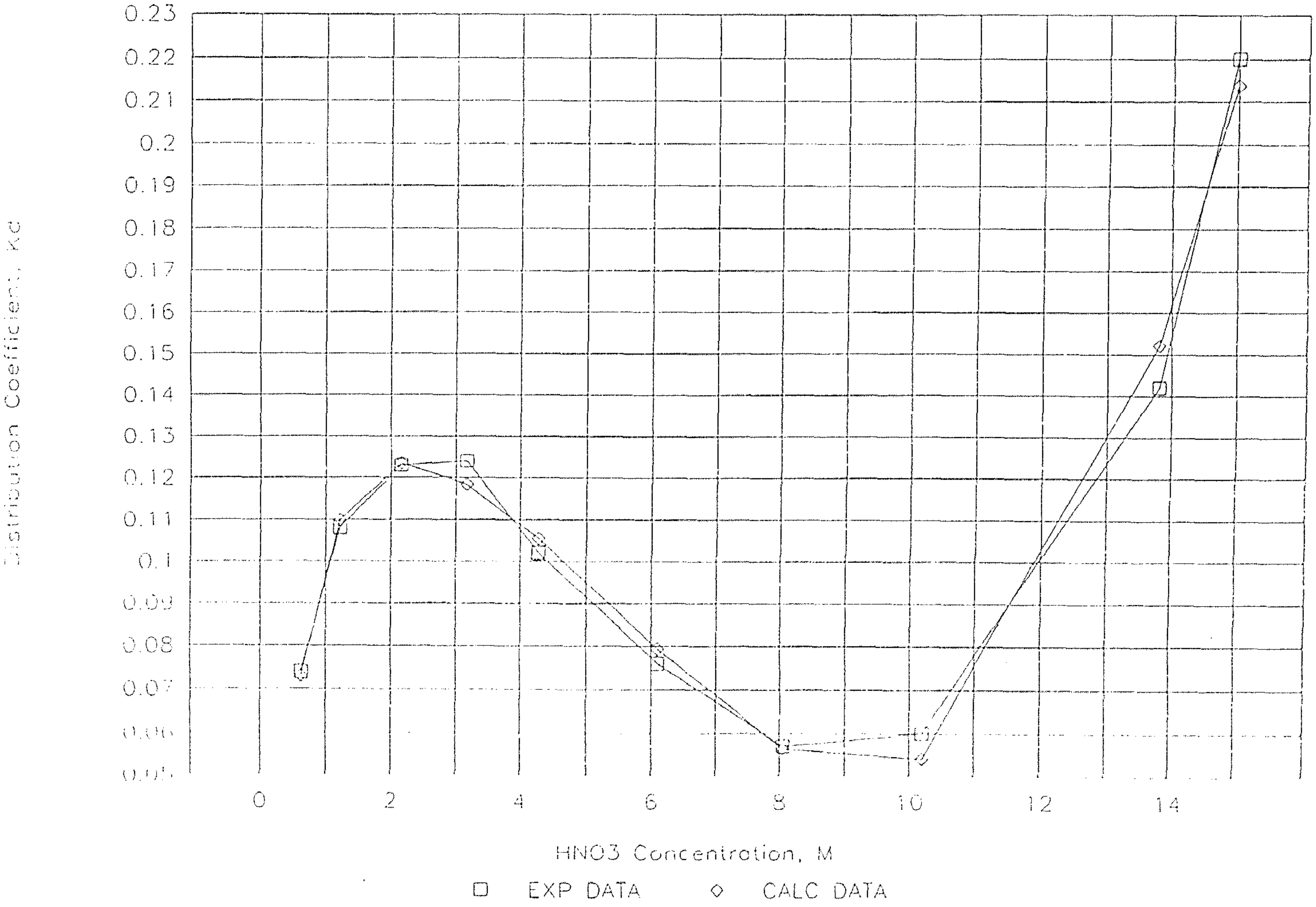

Figure 5.16 Comparison of the Experimental and Predicted Distribution Coefficients of Lanthanum.

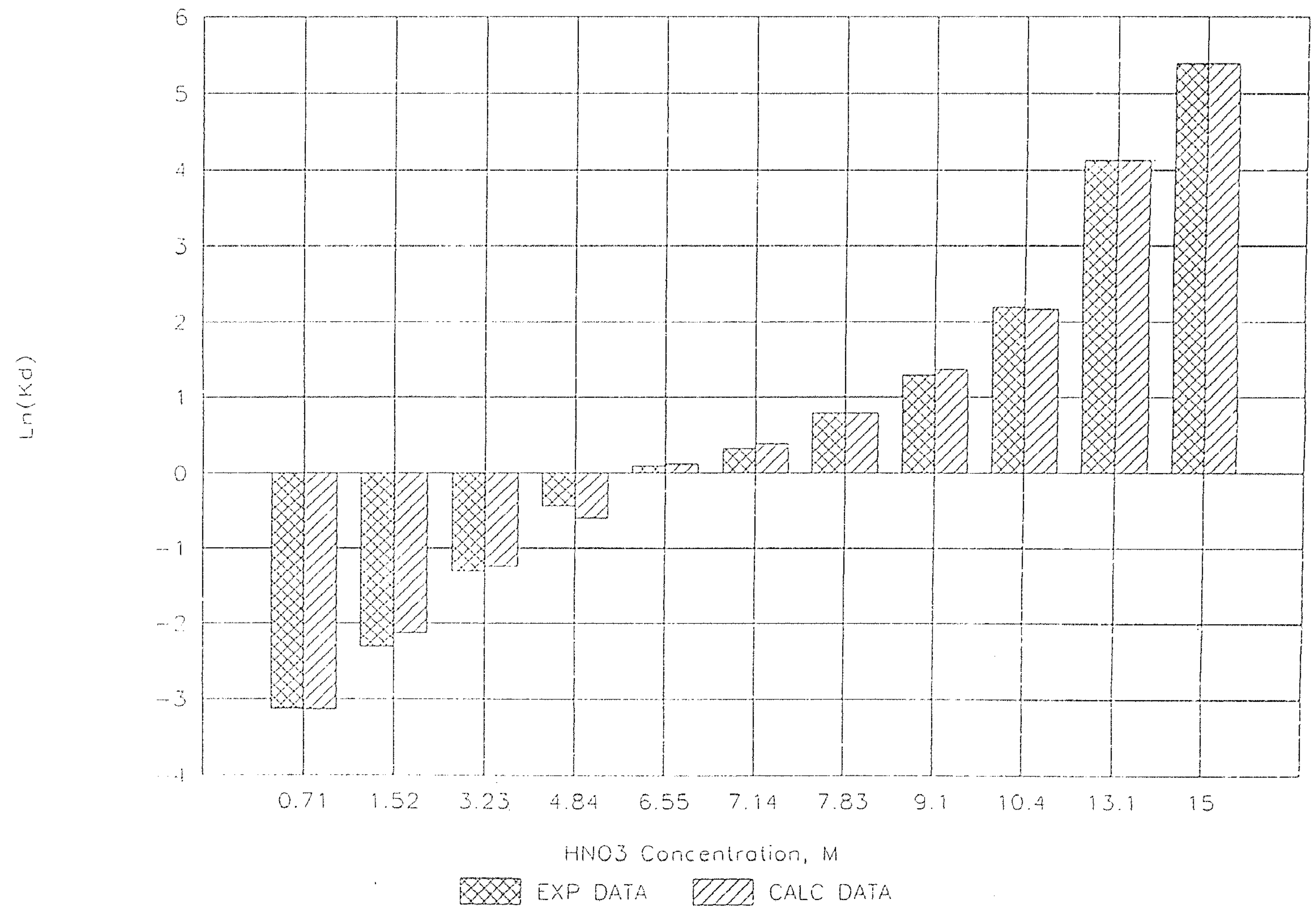

Figure 5.18 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Yttrium.

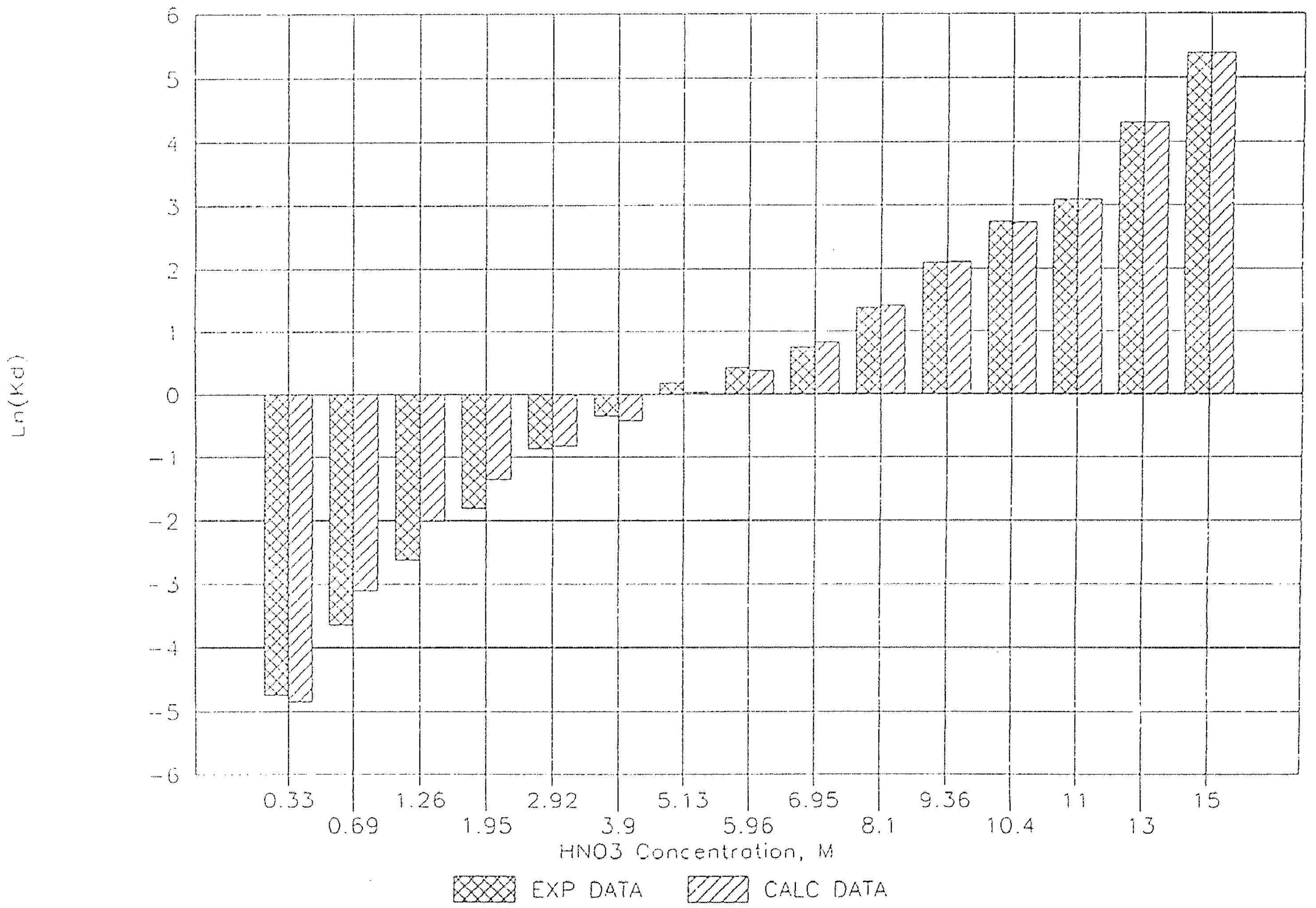

Figure 5.19 Bar Chart Comparison of the Experimenta and Predicted Distribution Coefficients of Ytterbium.

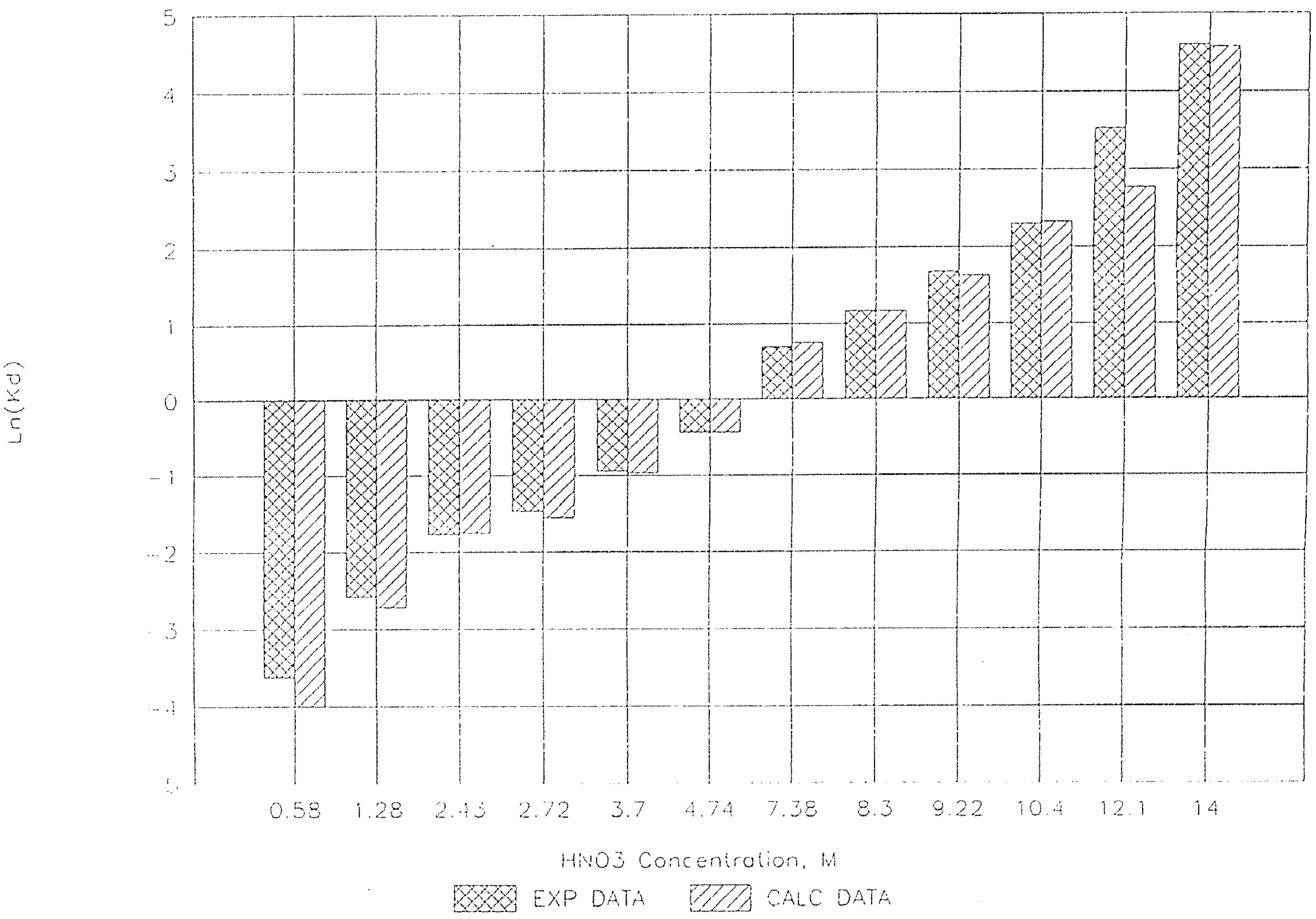

Figure 5.20 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Thulium.

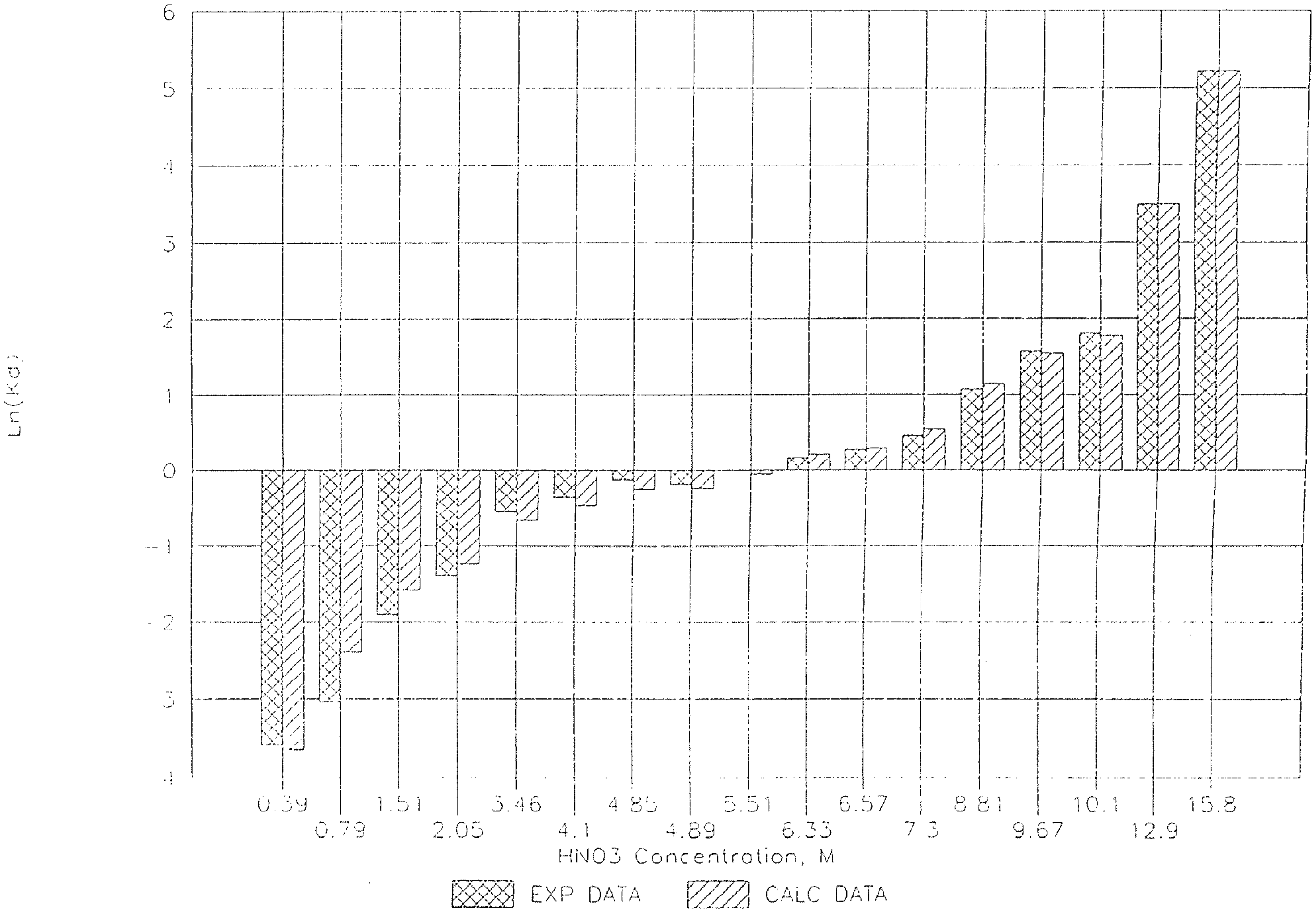

Figure 5.21 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Erbium.

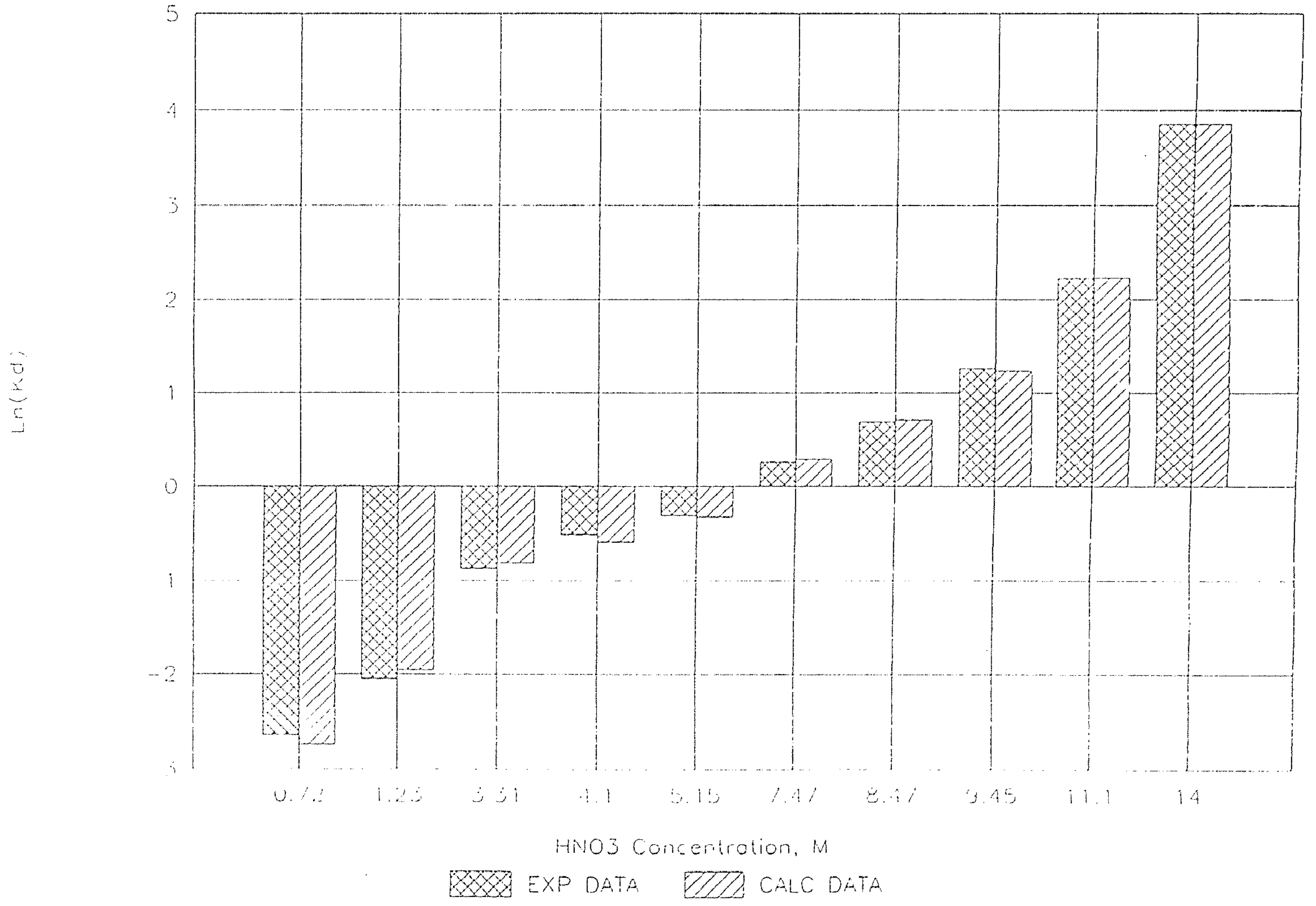

Figure 5.22 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Holmium.

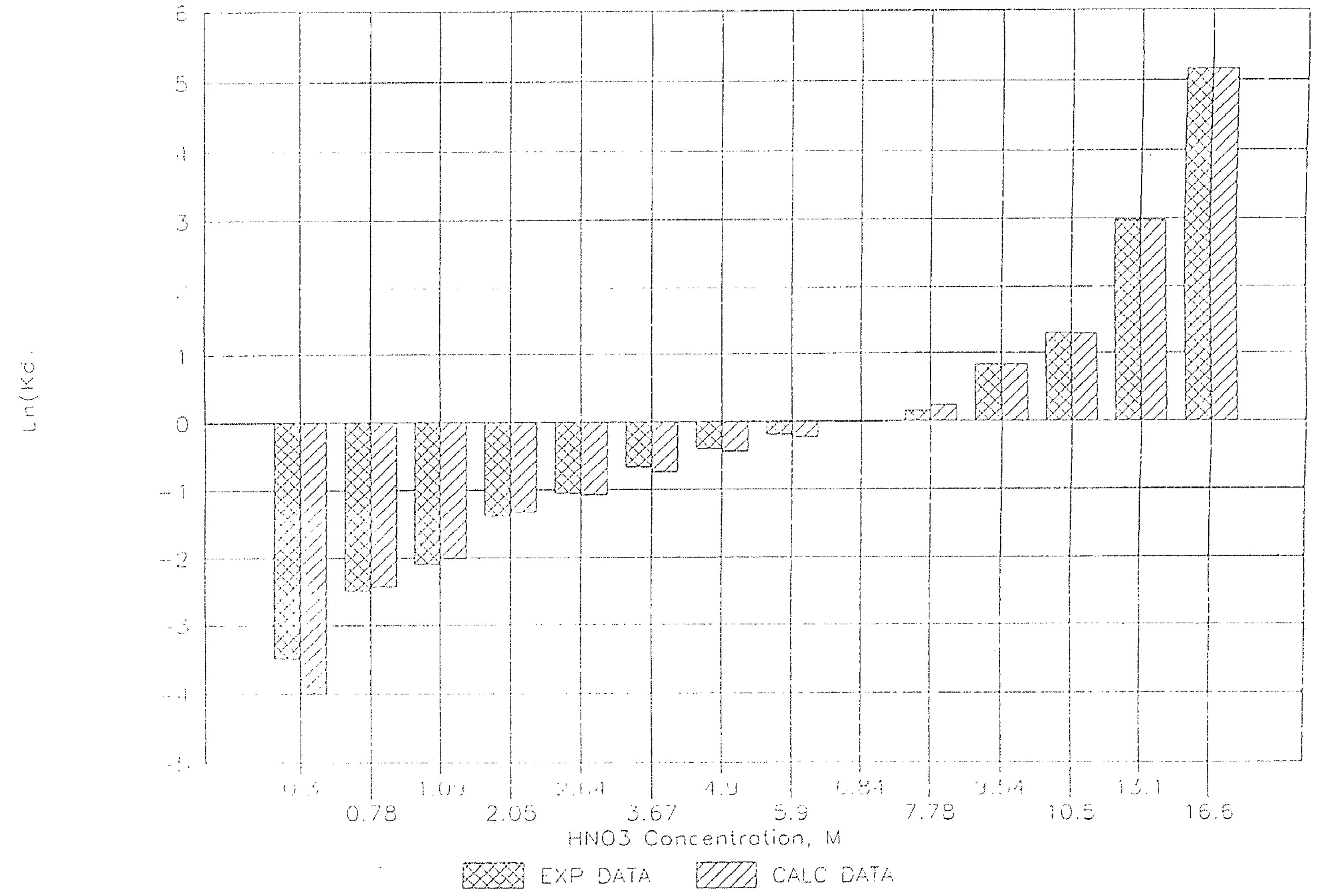

Figure 5.23 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Dysprosium.

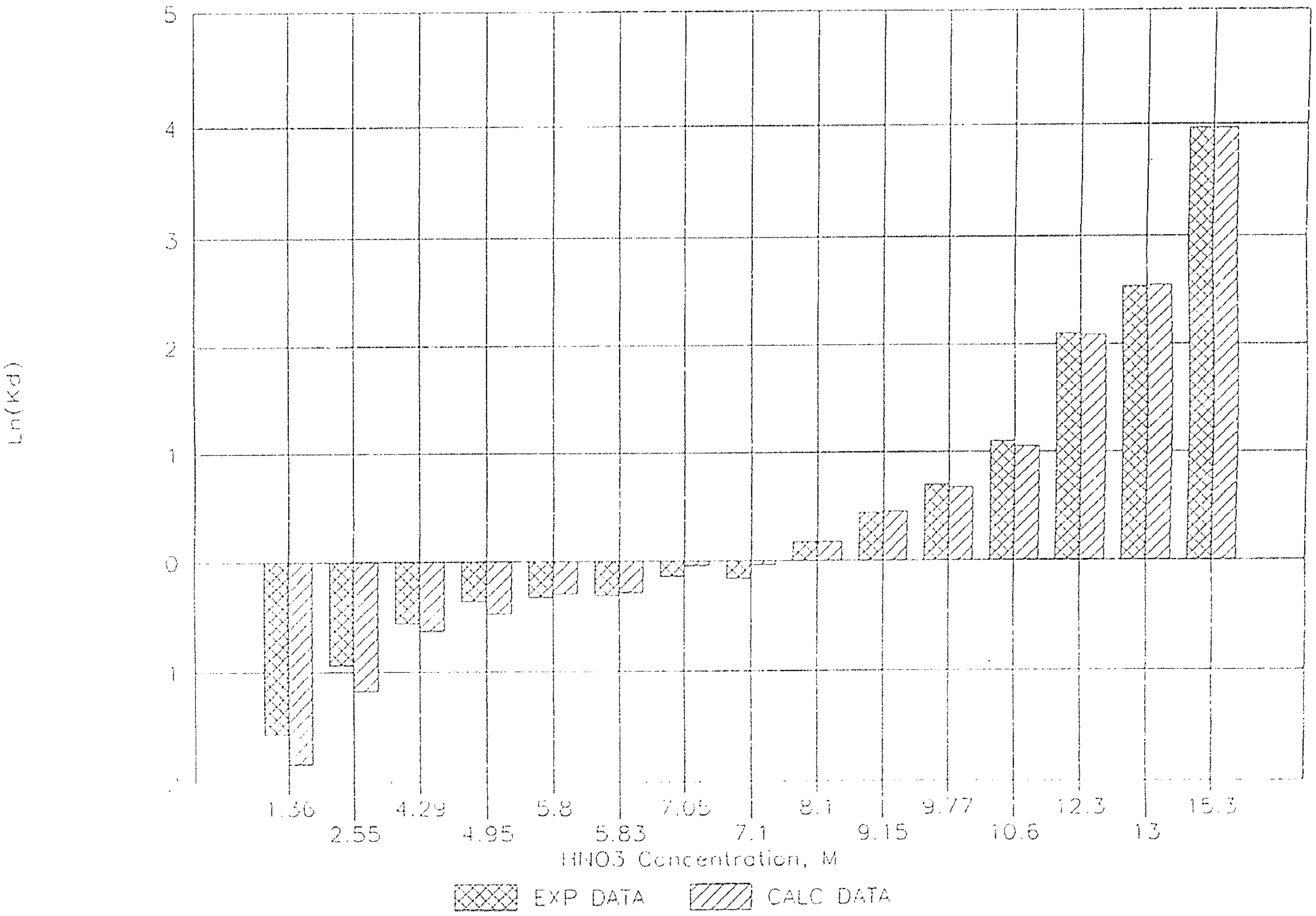

Figure 5.24 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Terbium.

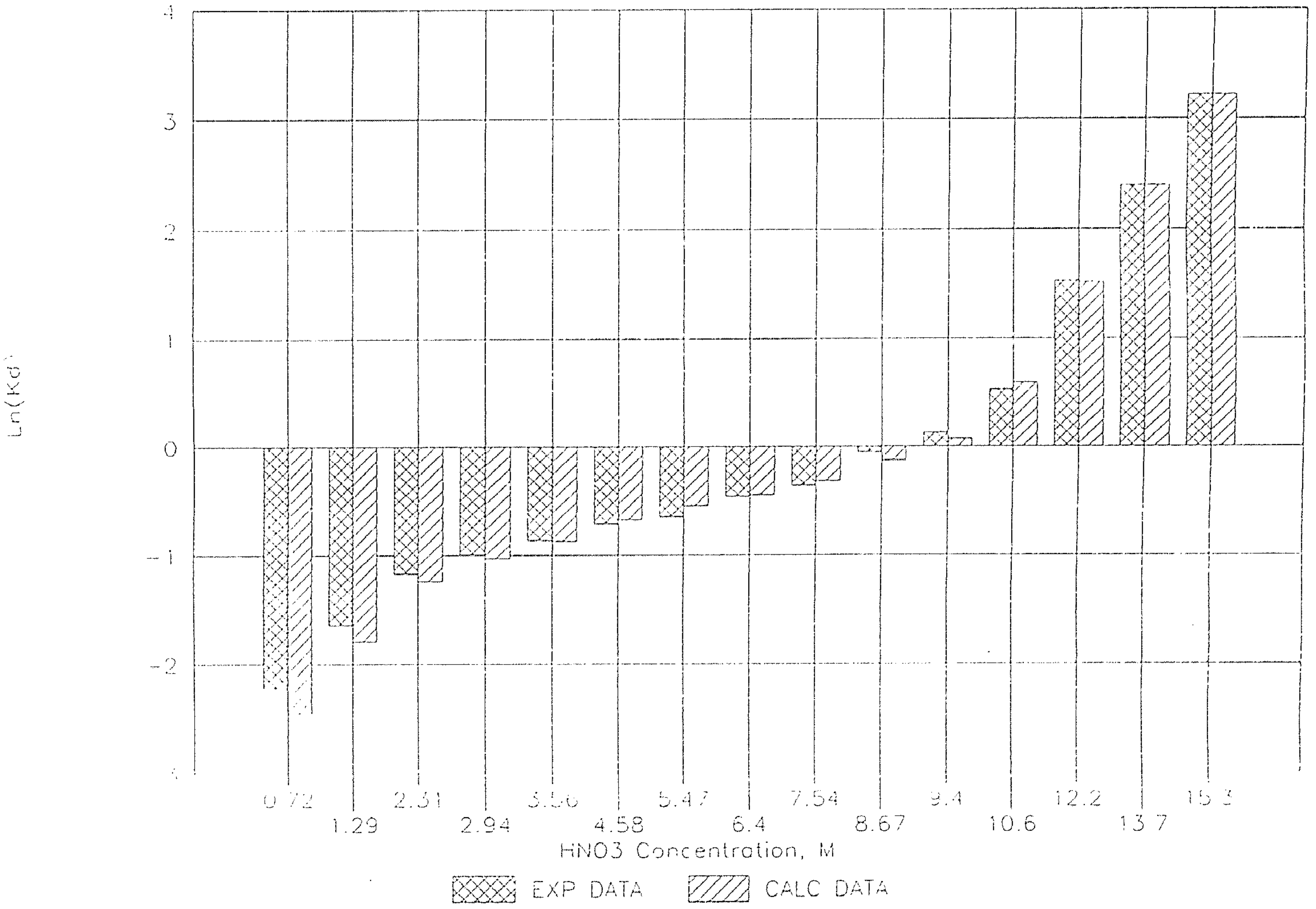

Figure 5.25 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Gadolinium.

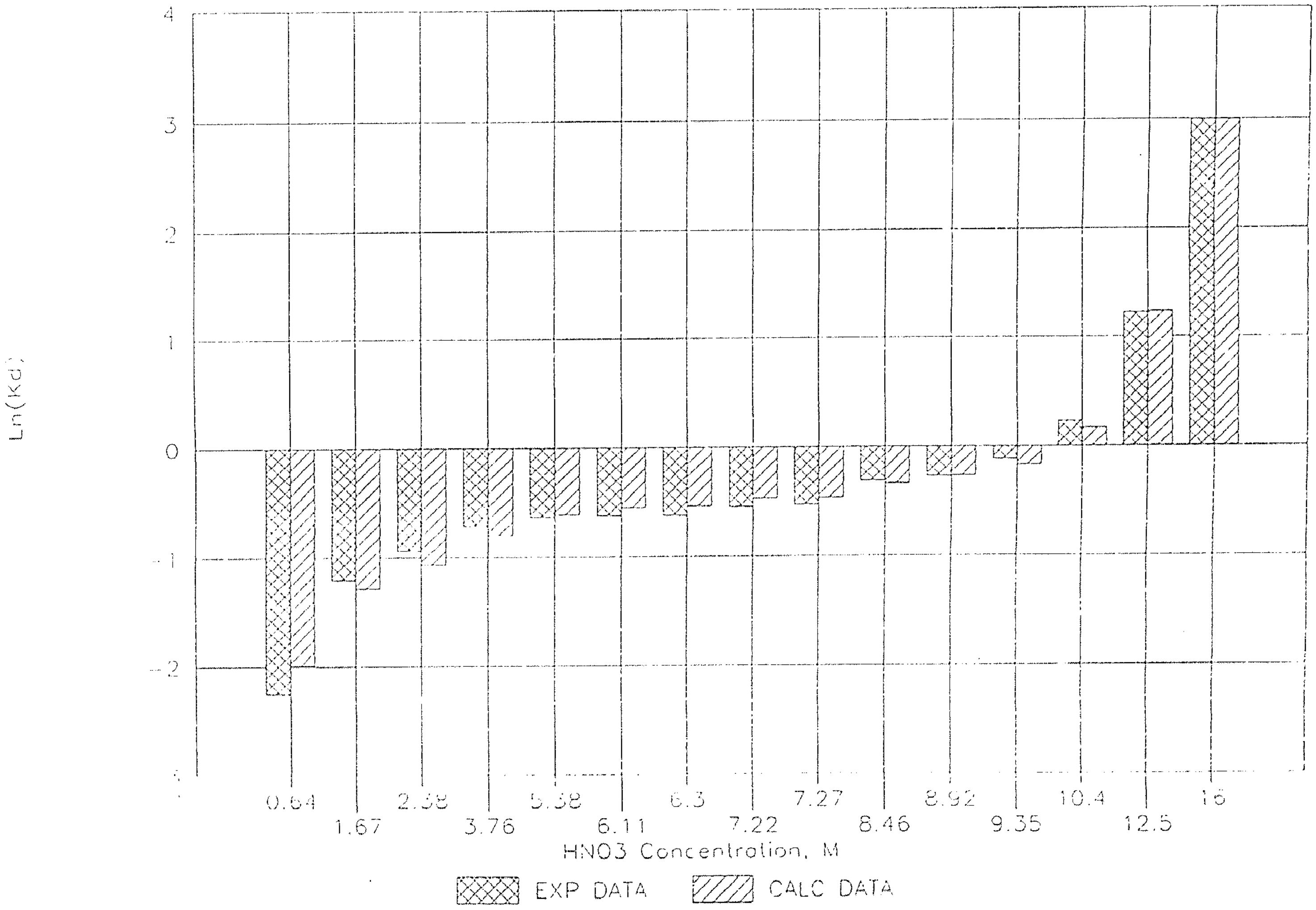

Figure 5.26 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Europium.

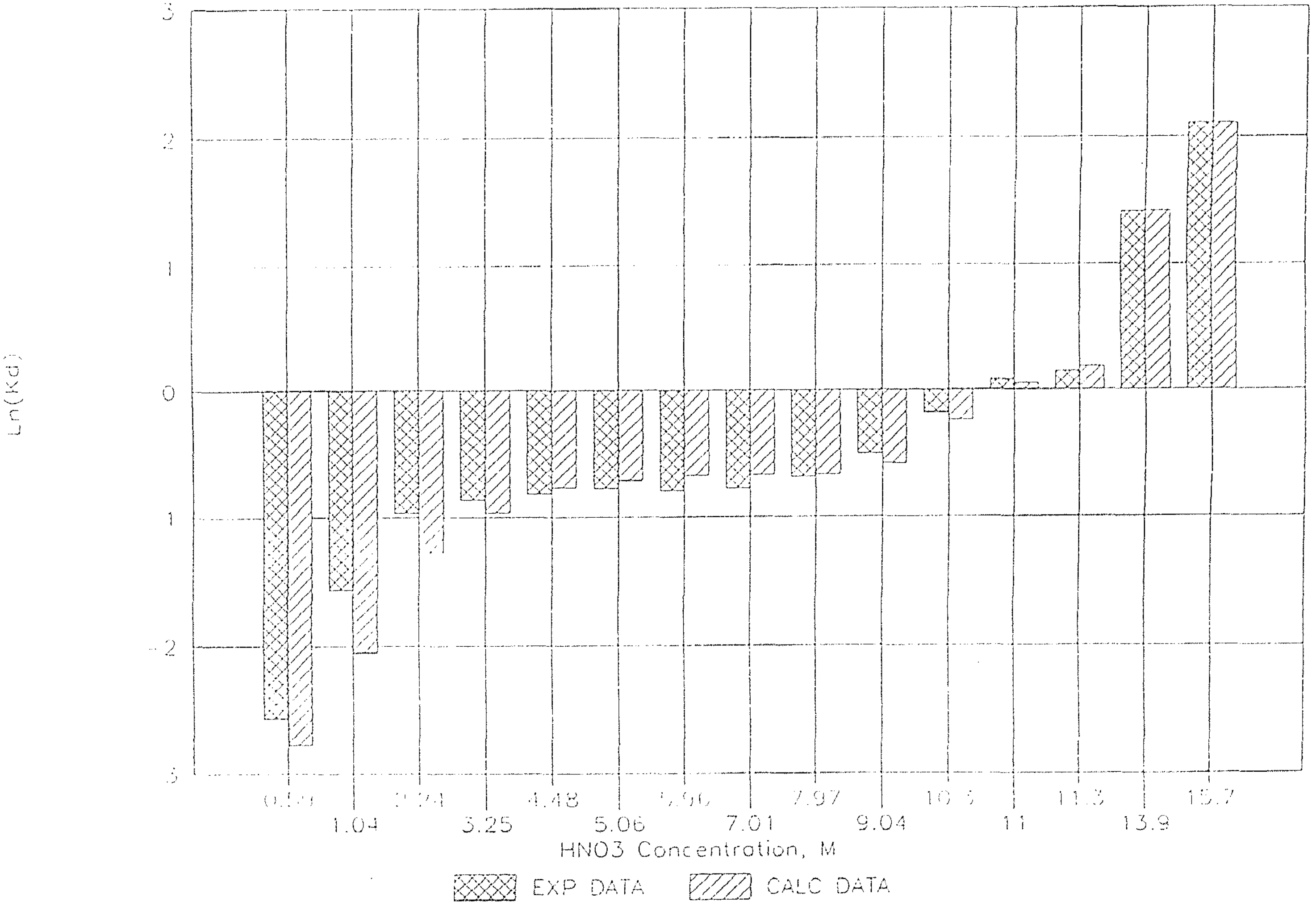

Figure 5.27 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Samarium.

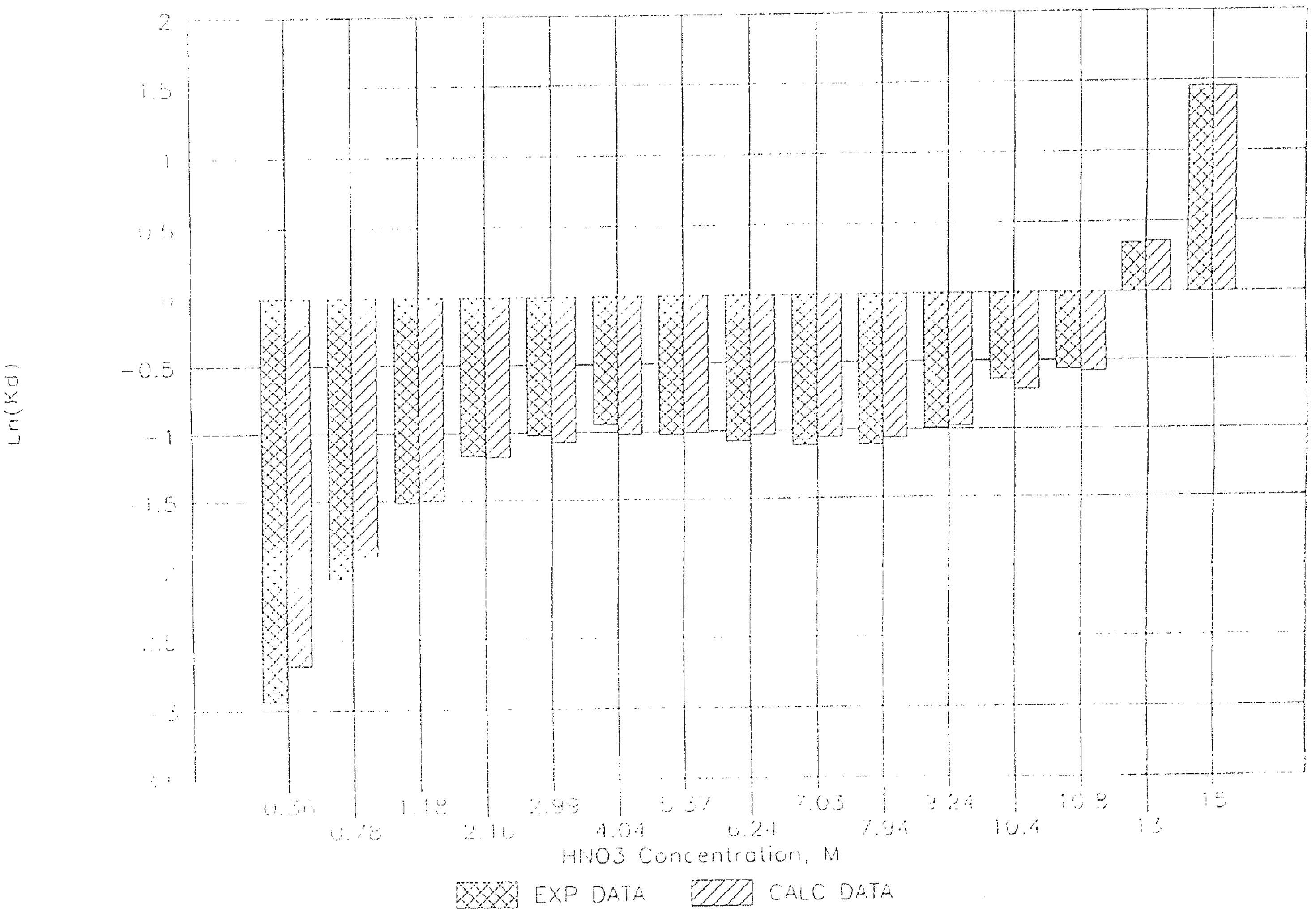

Figure 5.28 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Promethium.

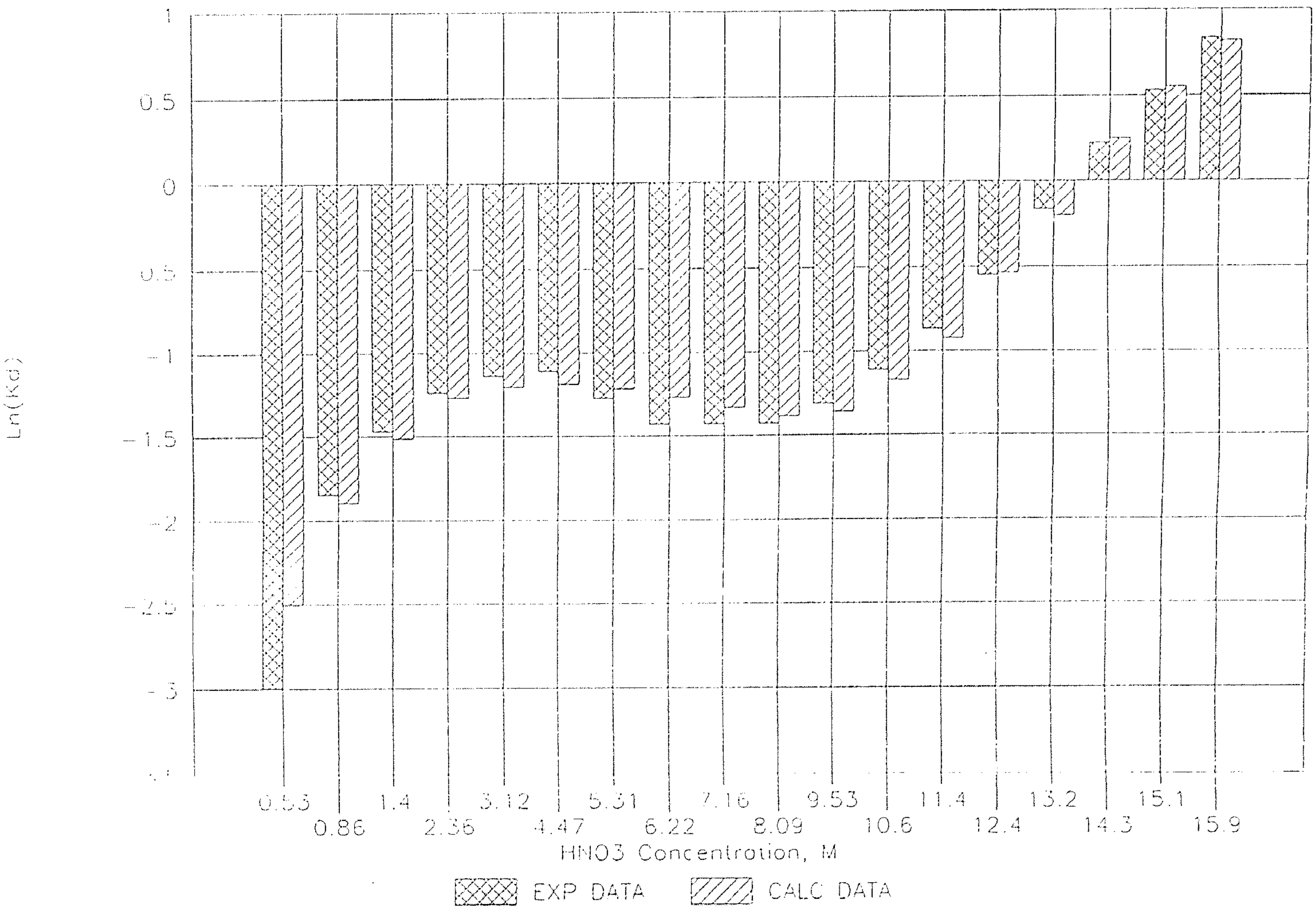

Figure 5.29 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Neodymium.

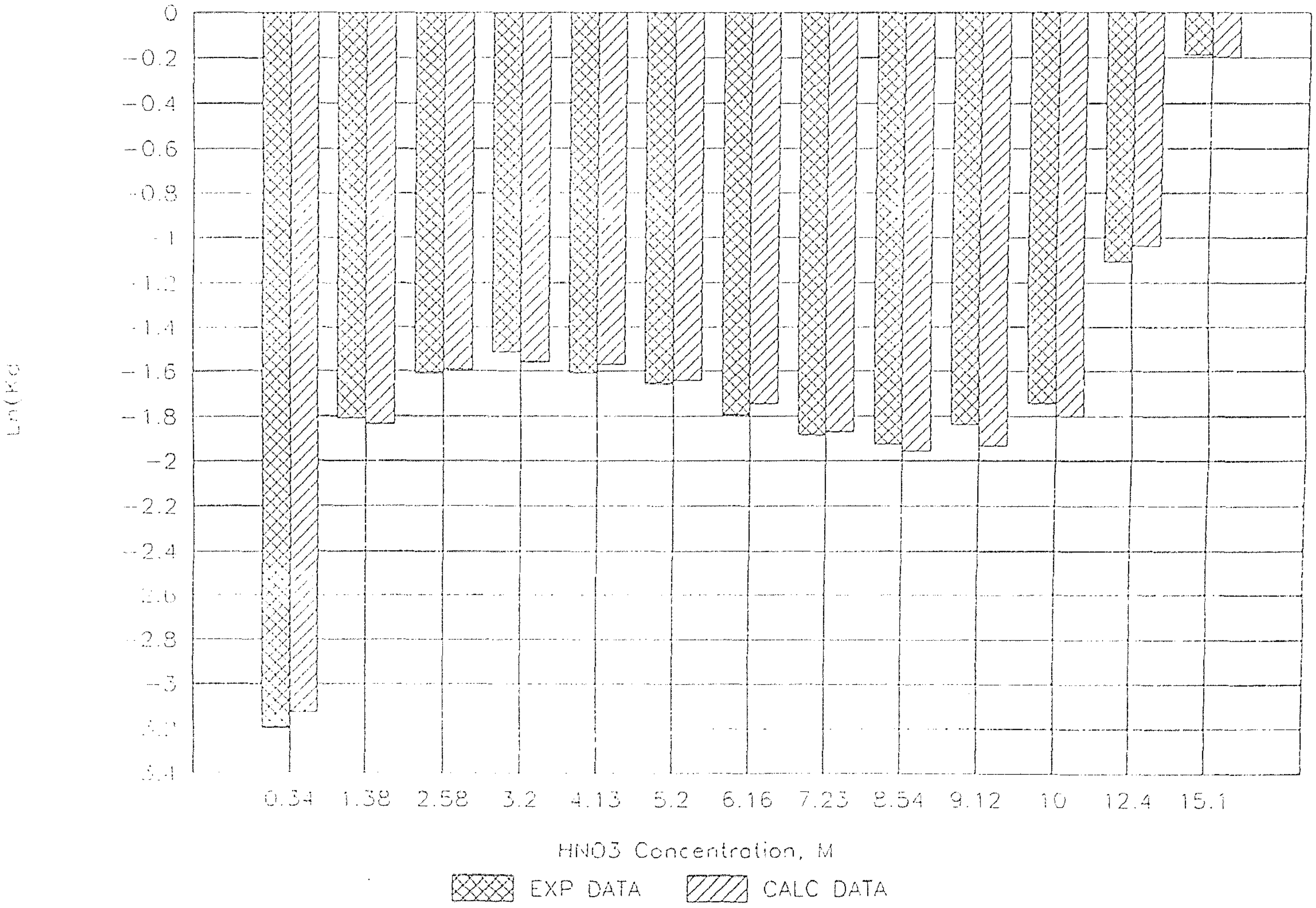

Figure 5.30 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Praseodymium.

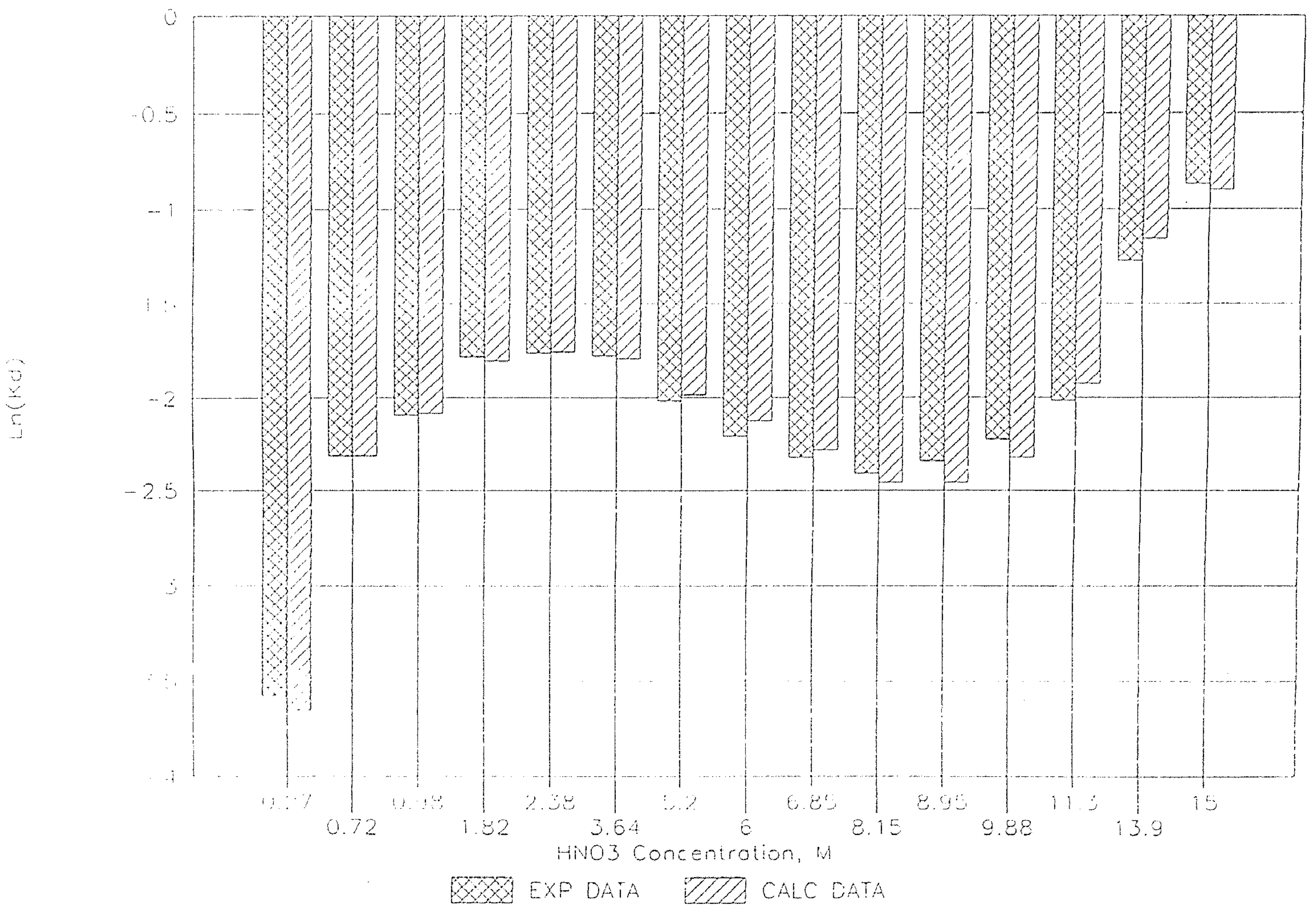

Figure 5.31 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Cerium.

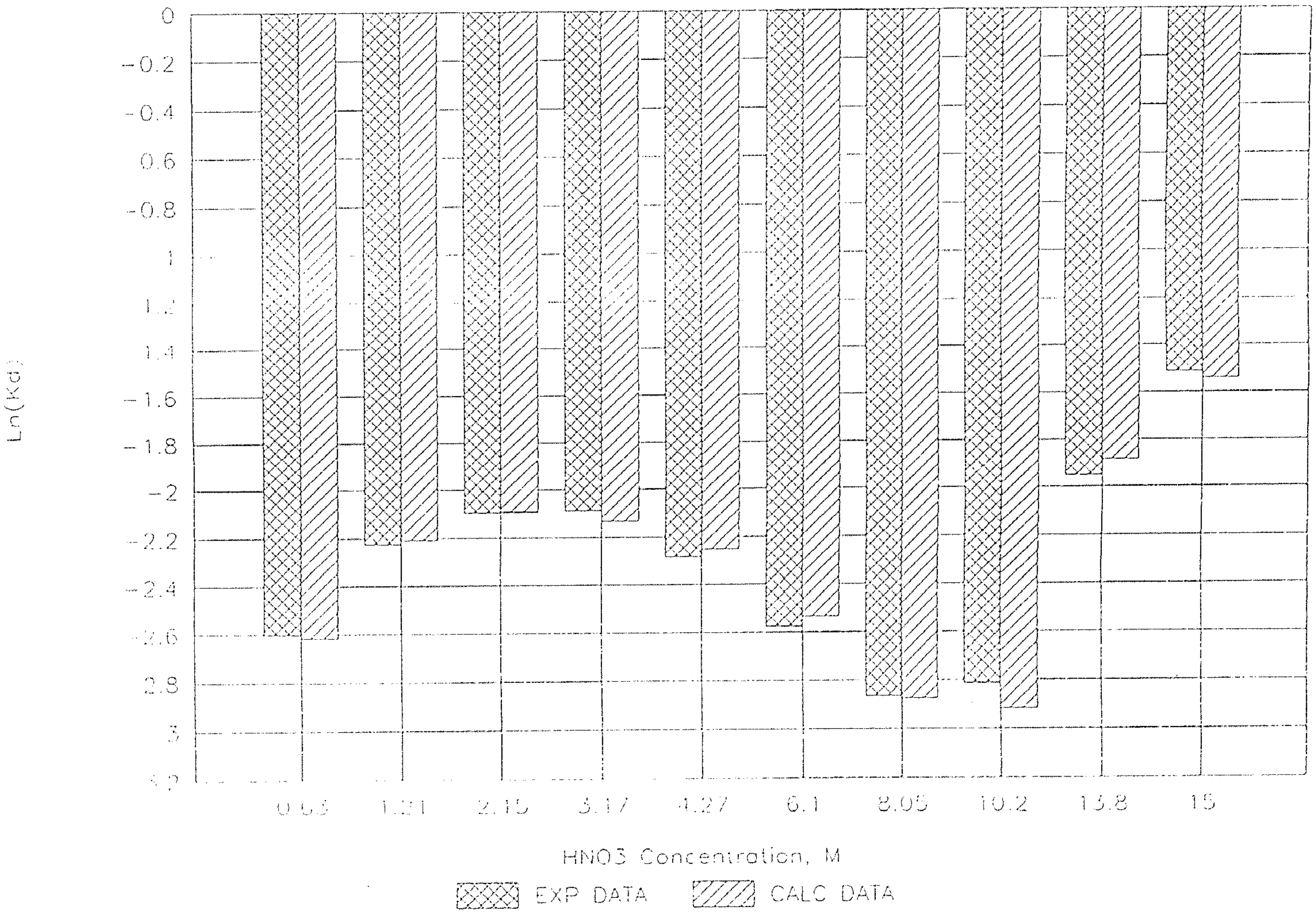

Figure 5.32 Bar Chart Comparison of the Experimental and Predicted Distribution Coefficients of Lanthanum.

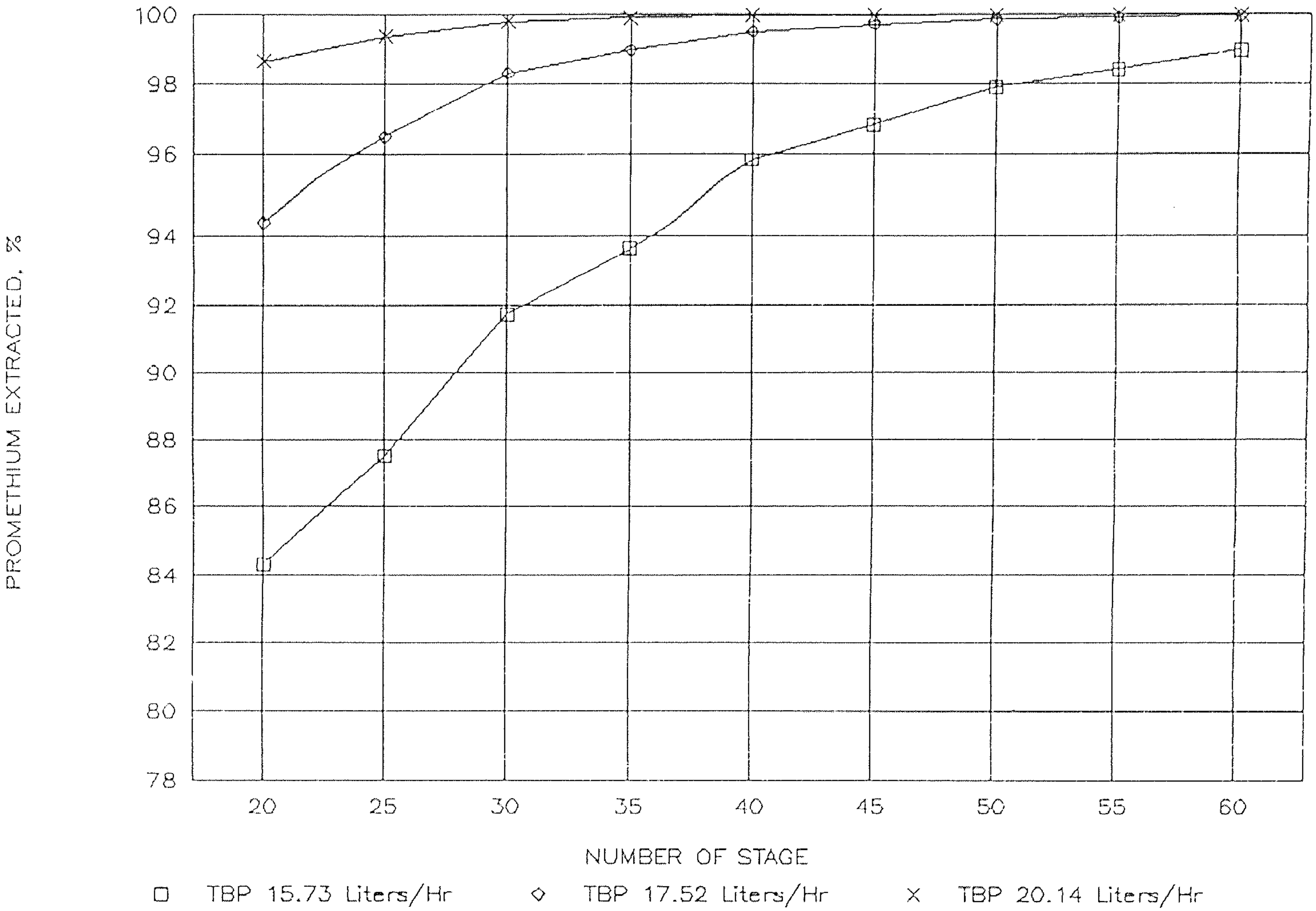

Figure 5.34 The Effect of Number of Stages on Promethium Extraction HNO_3 12.0 N.

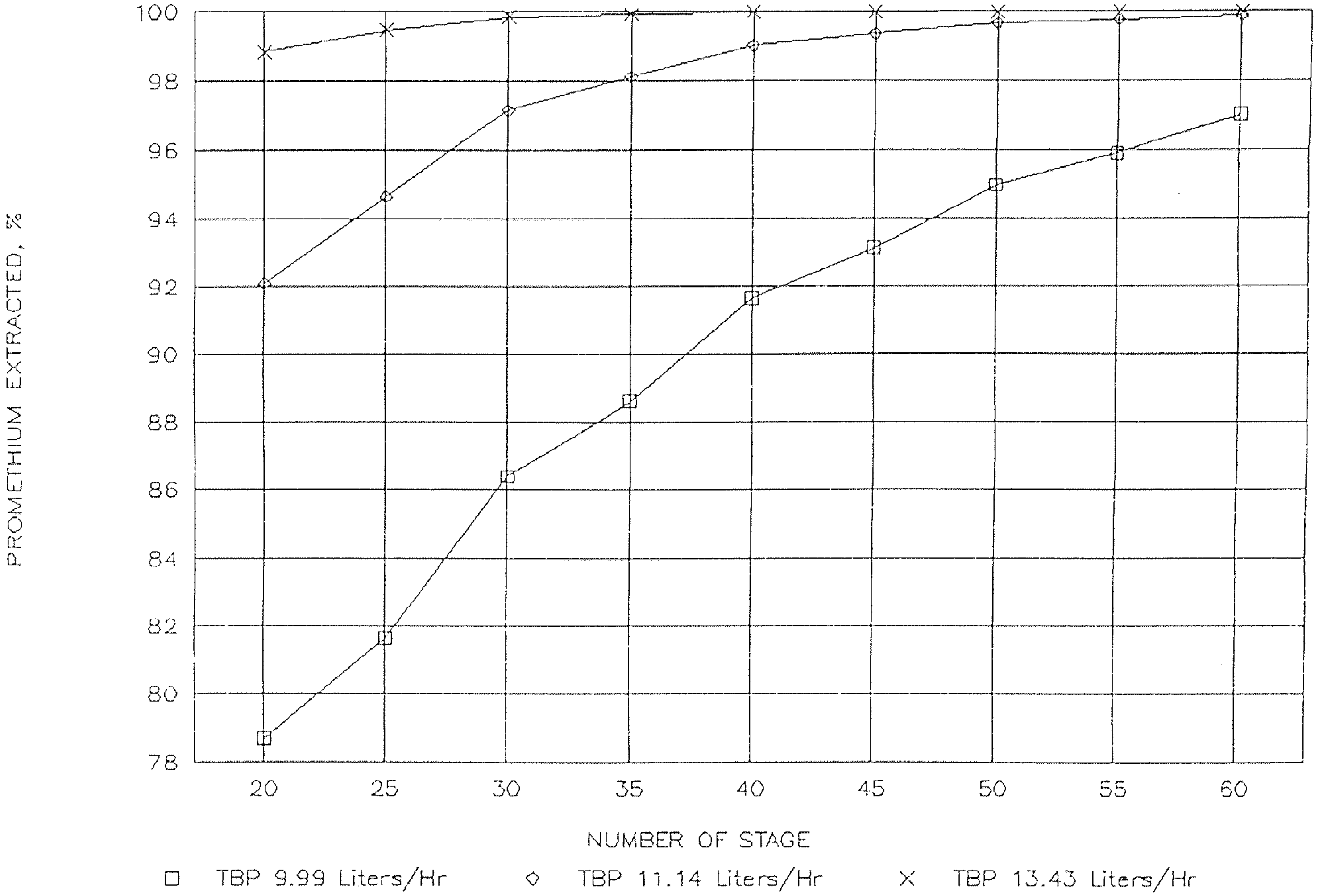

Figure 5.35 The Effect of Number of Stages on Promethium Extraction HNO_3 13.0 N.

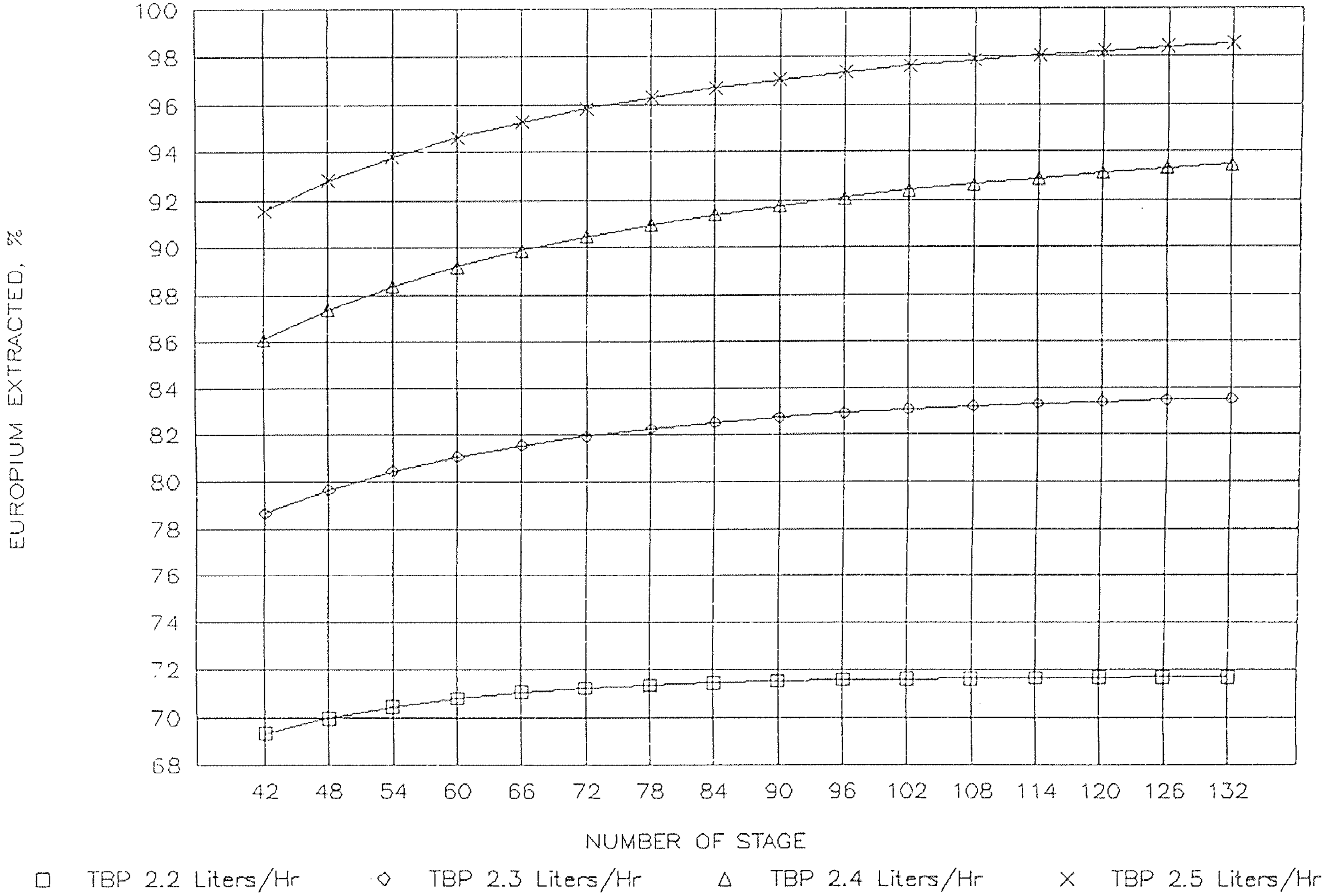

Figure 6.5 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO_3 9.9 N.

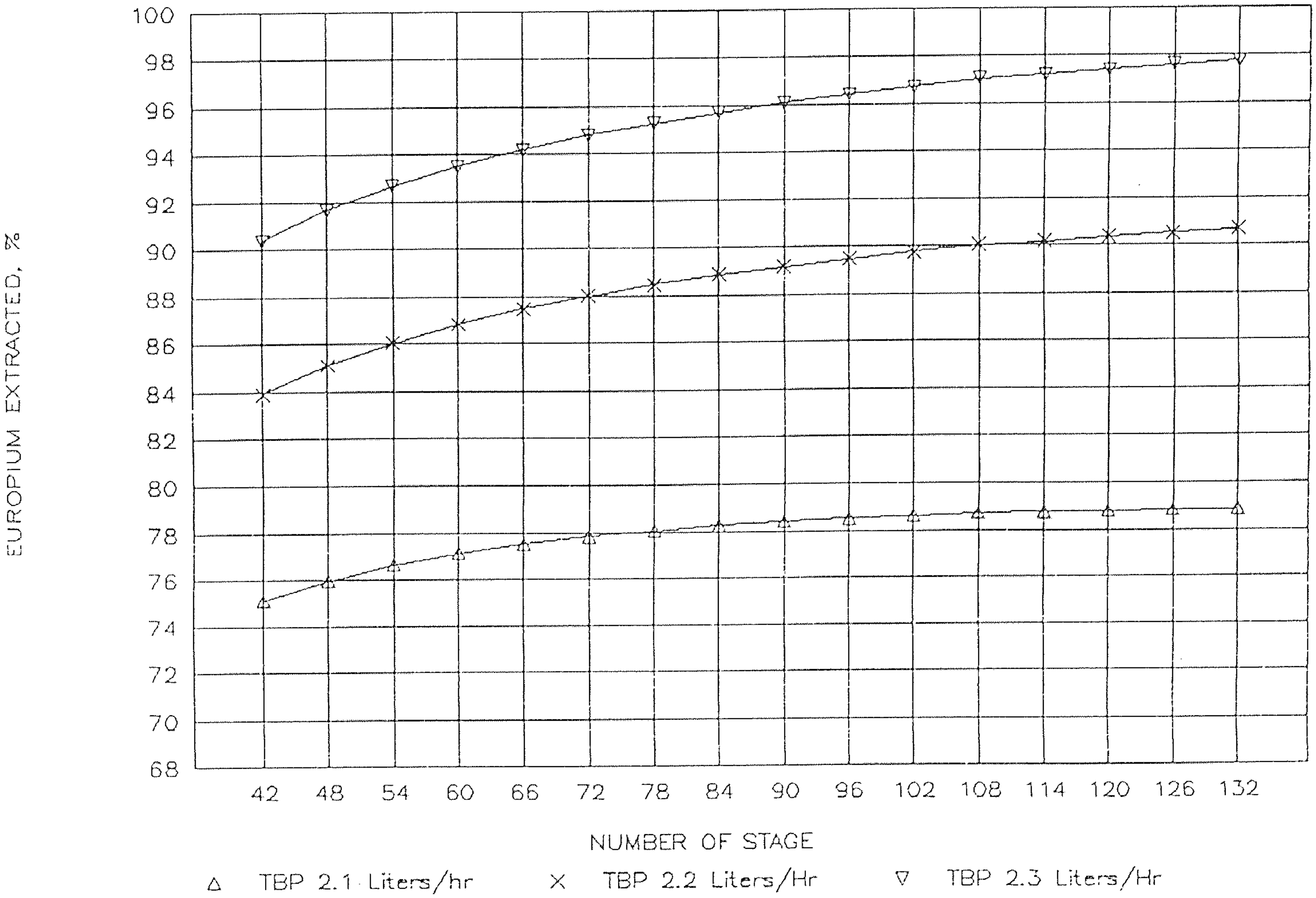

Figure 6.6 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO_3 10.0 N.

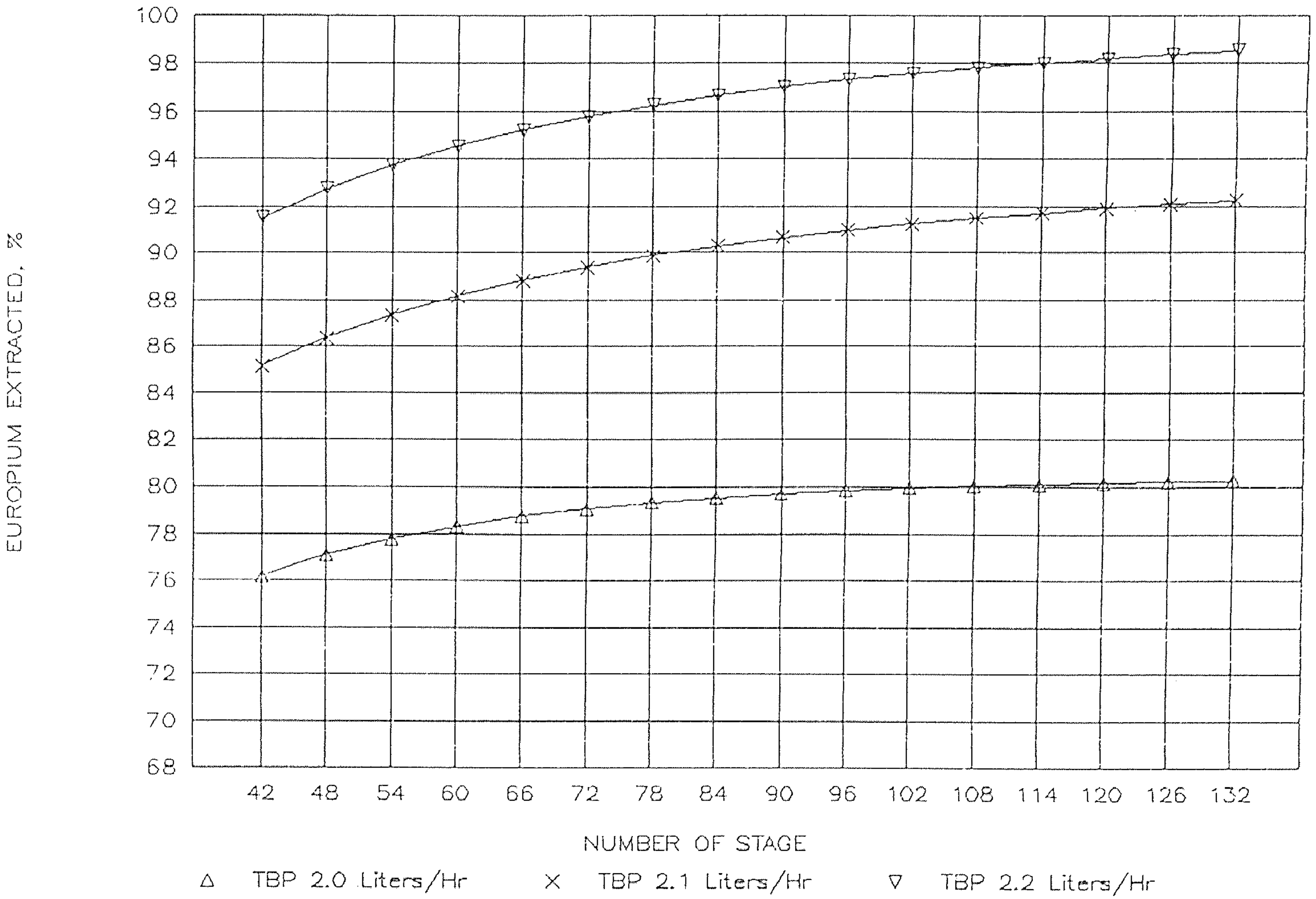

Figure 6.7 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO_3 10.1 N.

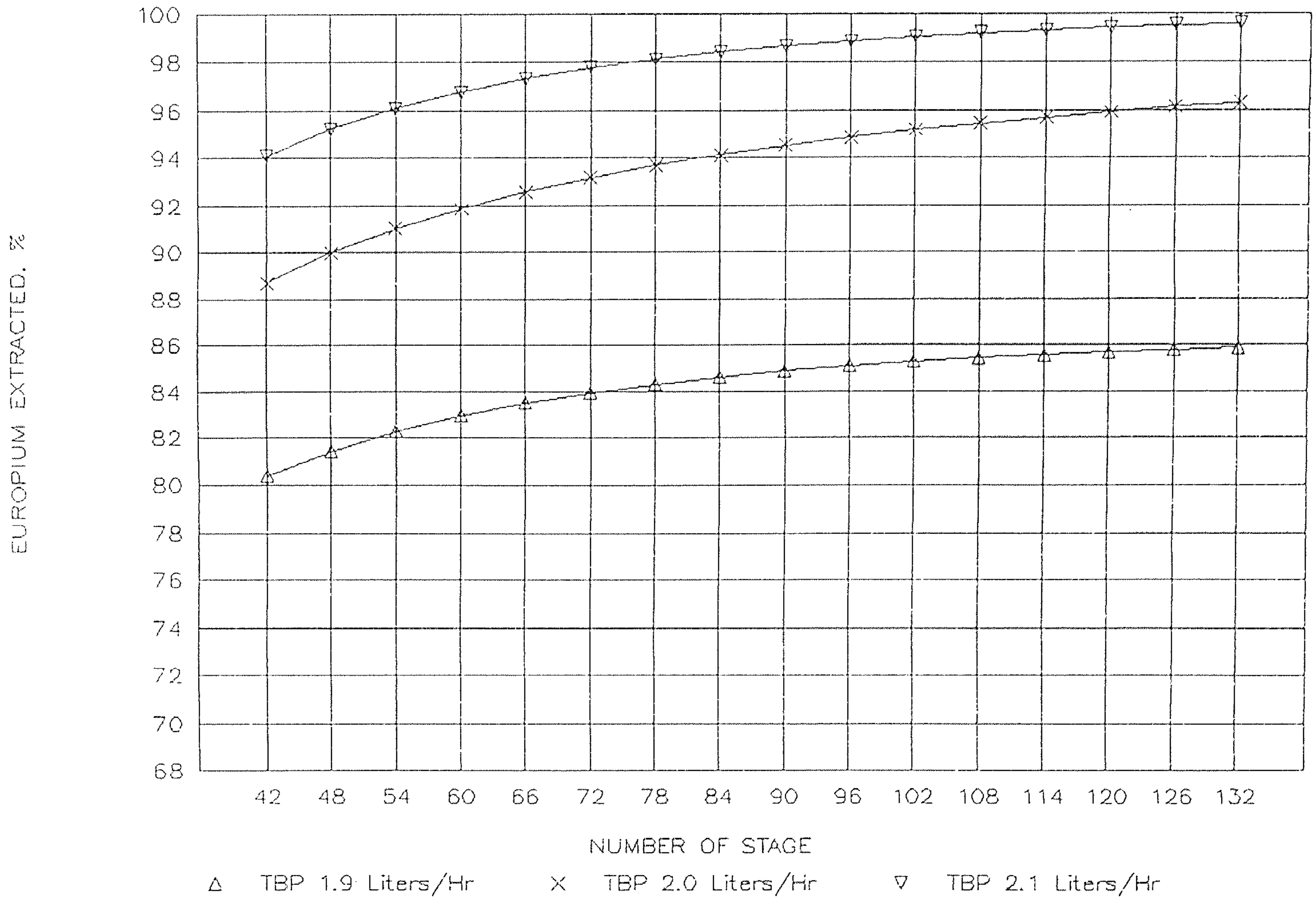

Figure 6.8 The Effect of Number of Stages on Europium Extraction, Europium Extracted %, HNO_3 10.2 N.

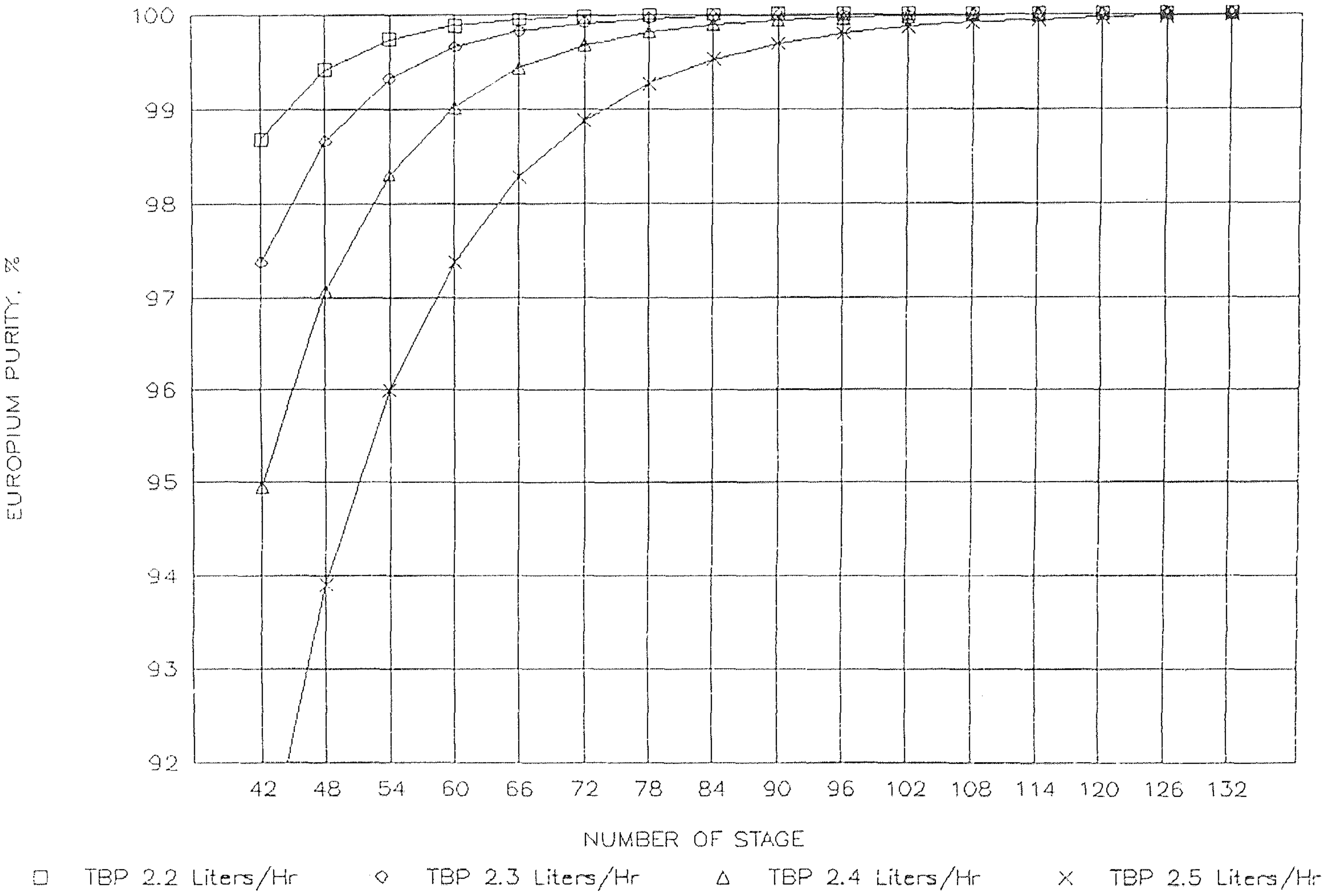

Figure 6.10 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 9.9 N.

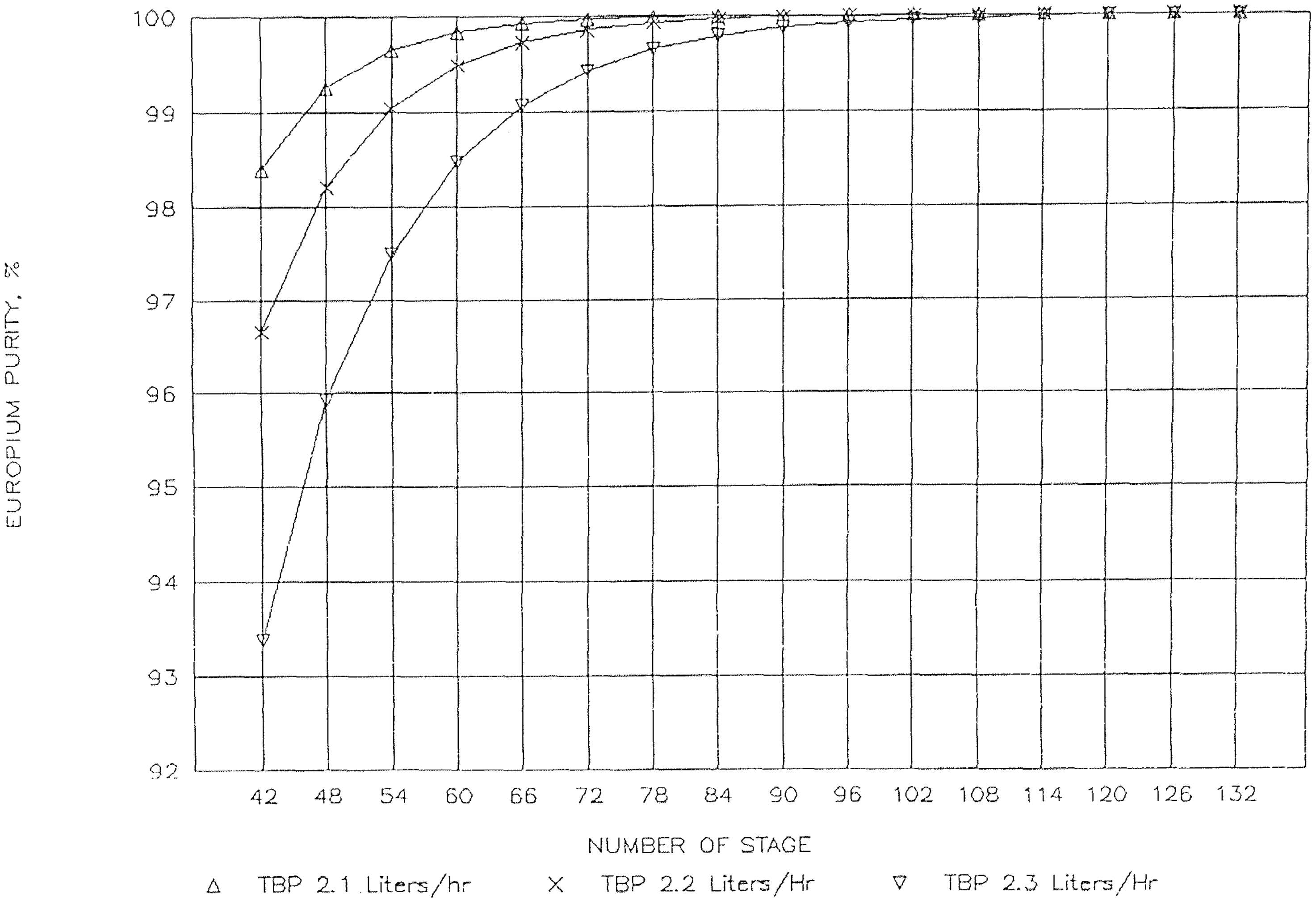

Figure 6.11 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 10.0 N.

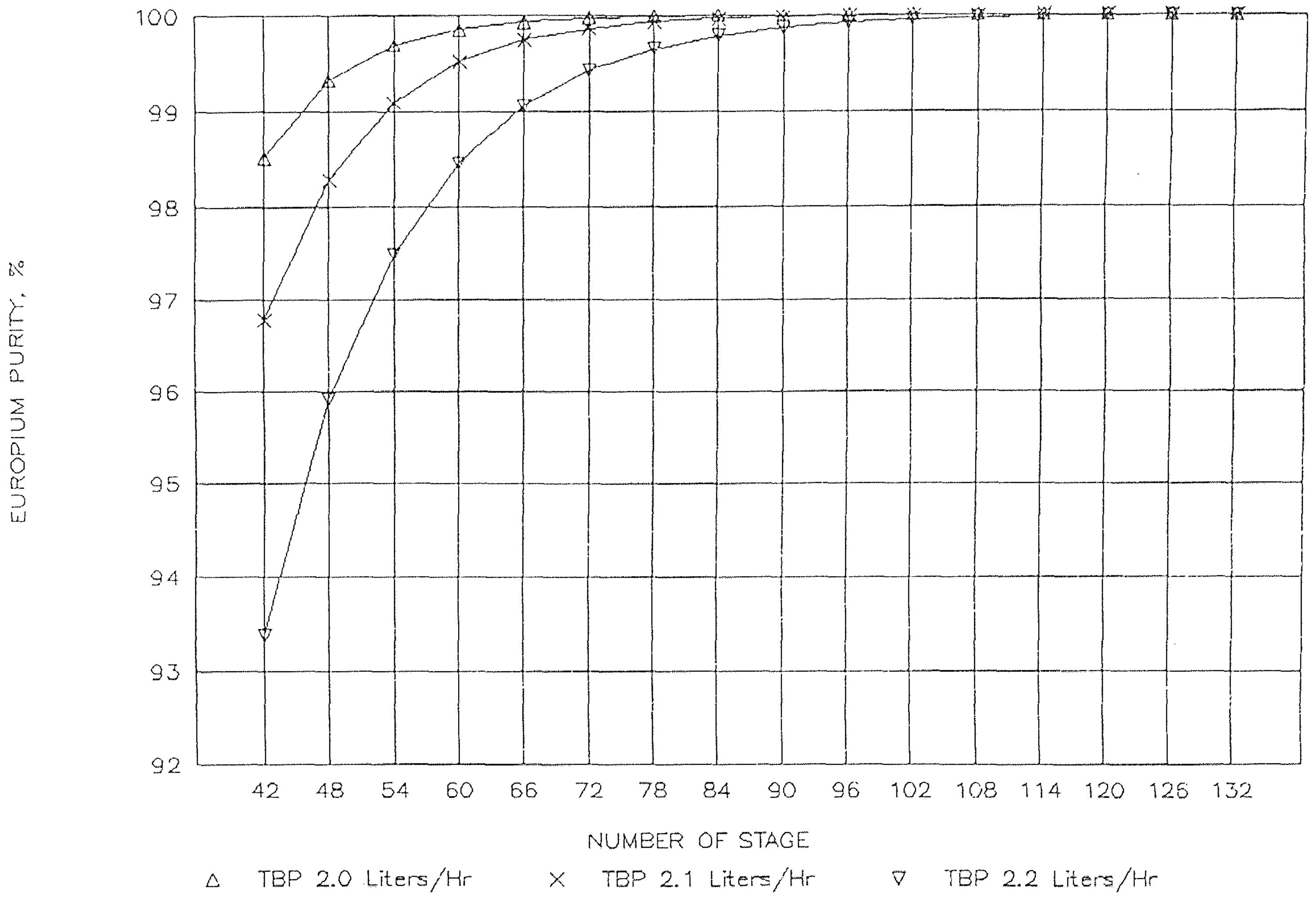

Figure 6.12 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 10.1 N.

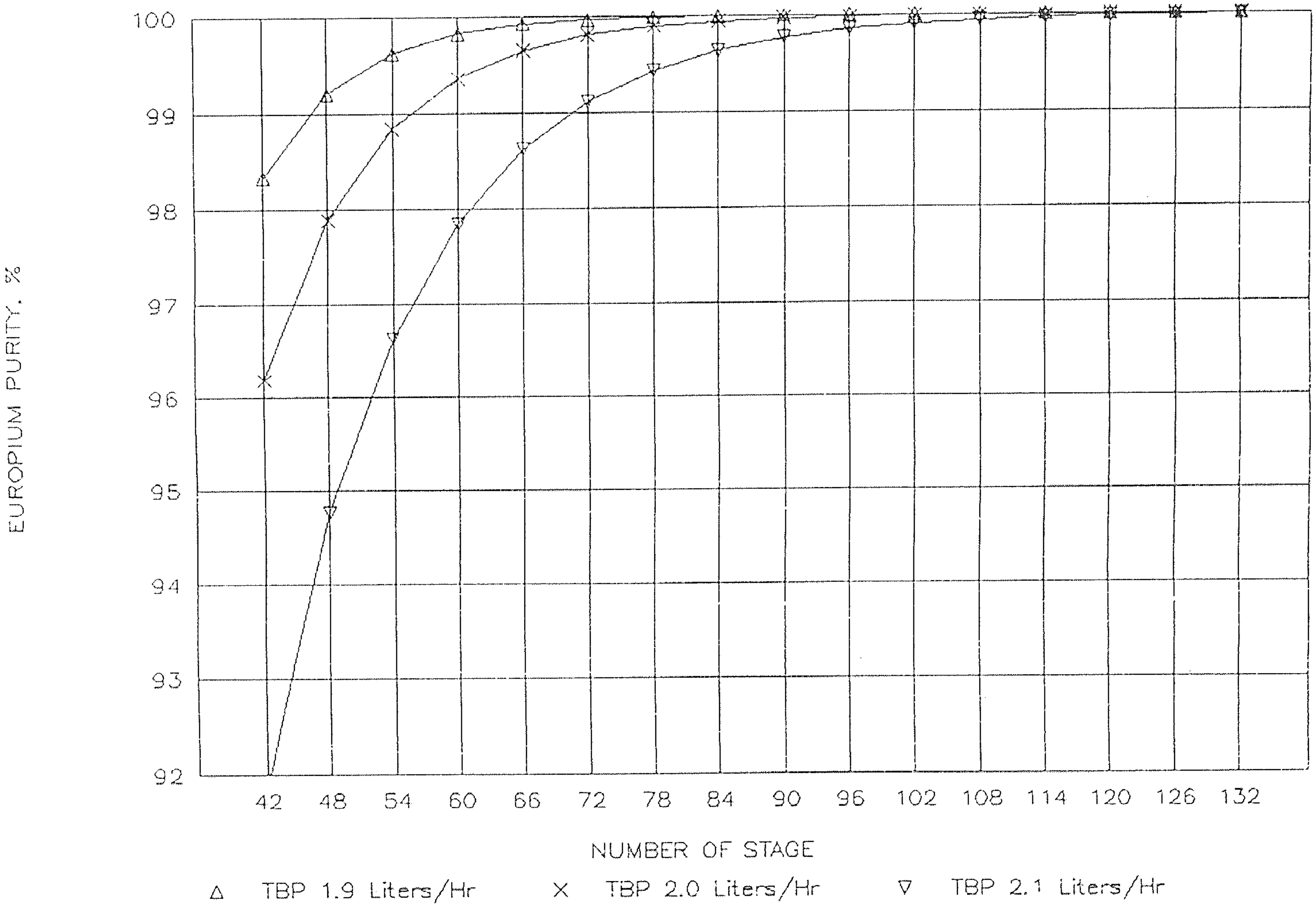

Figure 6.13 The Effect of Number of Stages on Europium Extraction, Europium Purity %, HNO_3 10.2 N.

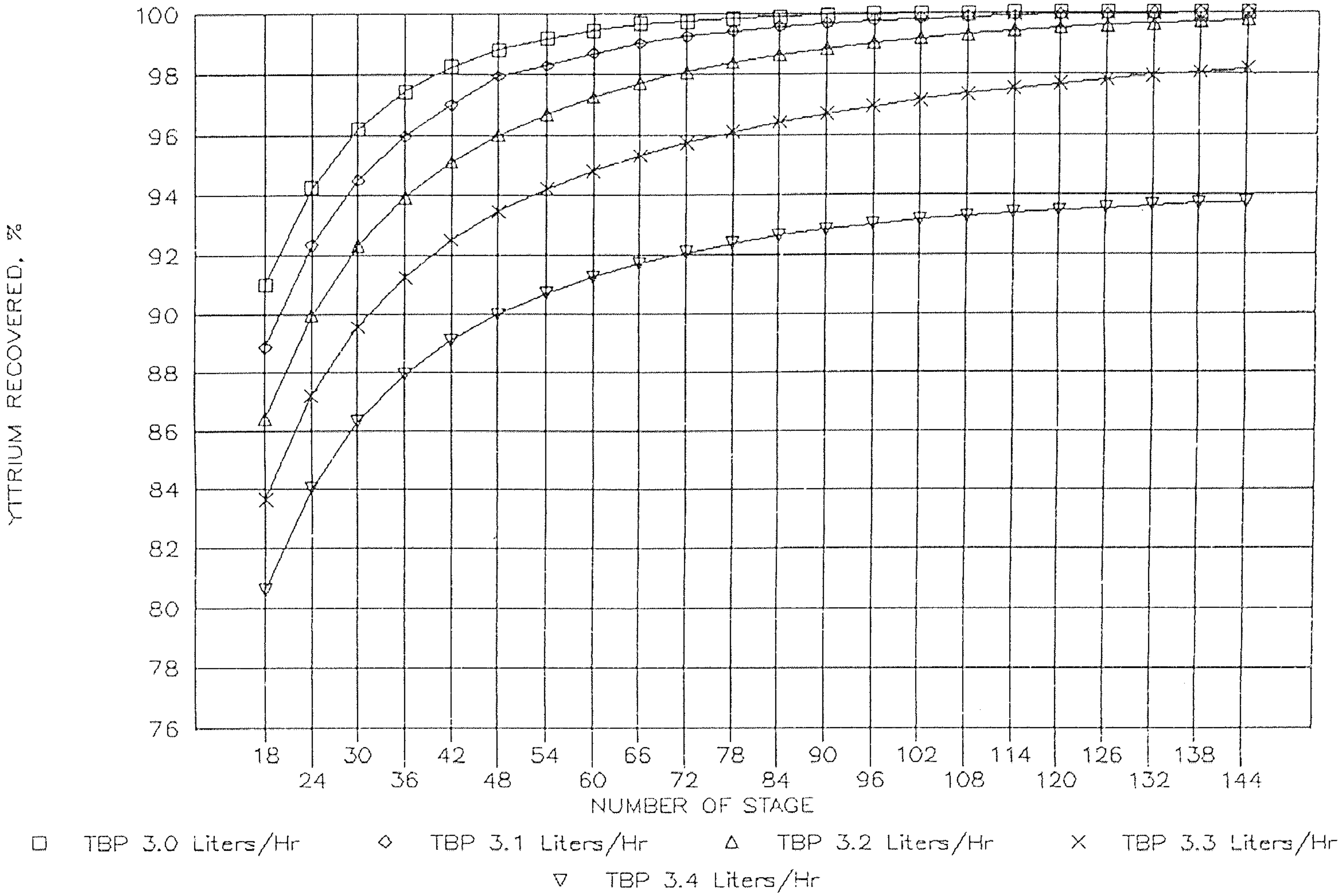

Figure 7.2 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO_3 6.2 N.

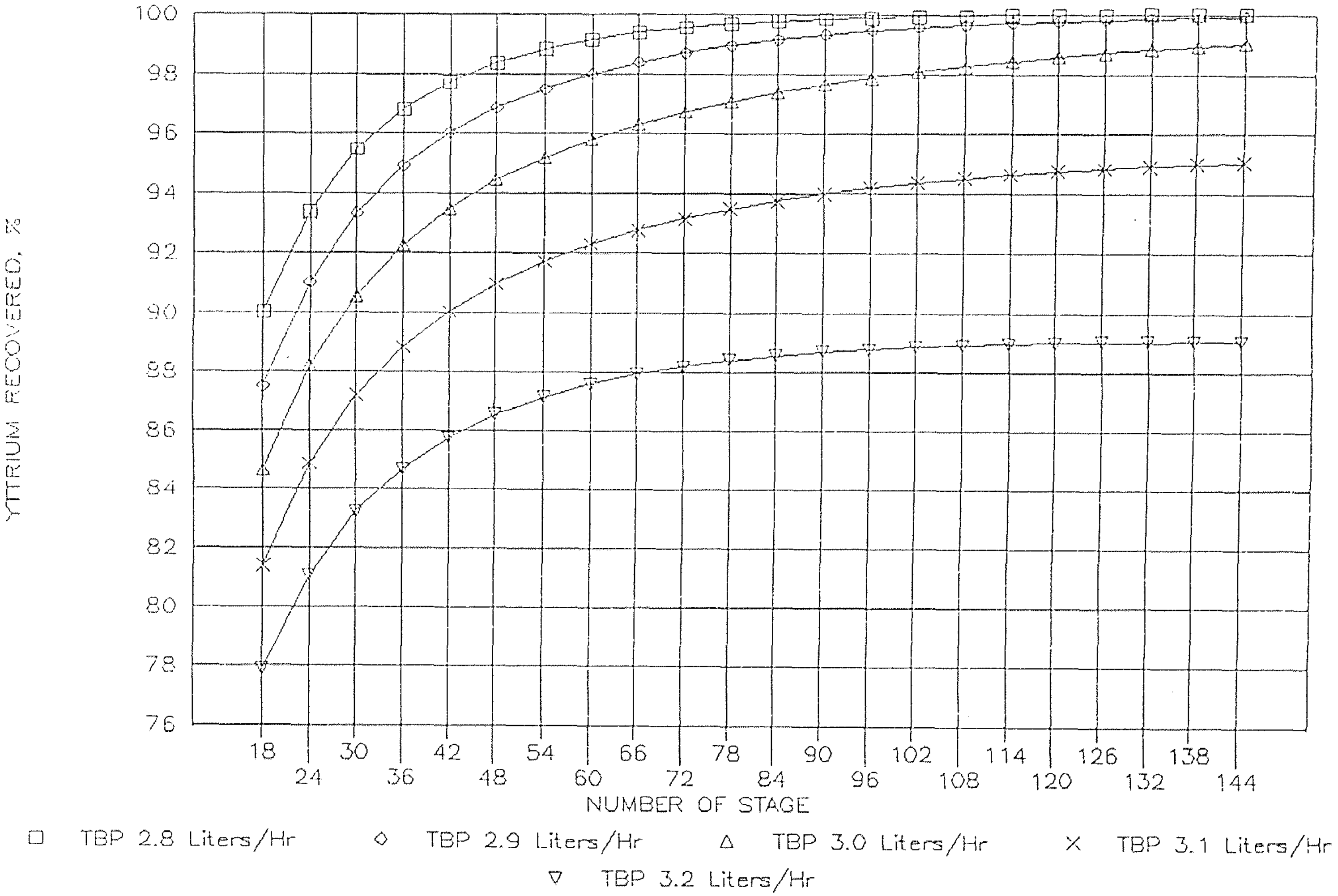

Figure 7.3 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO_3 6.3 N.

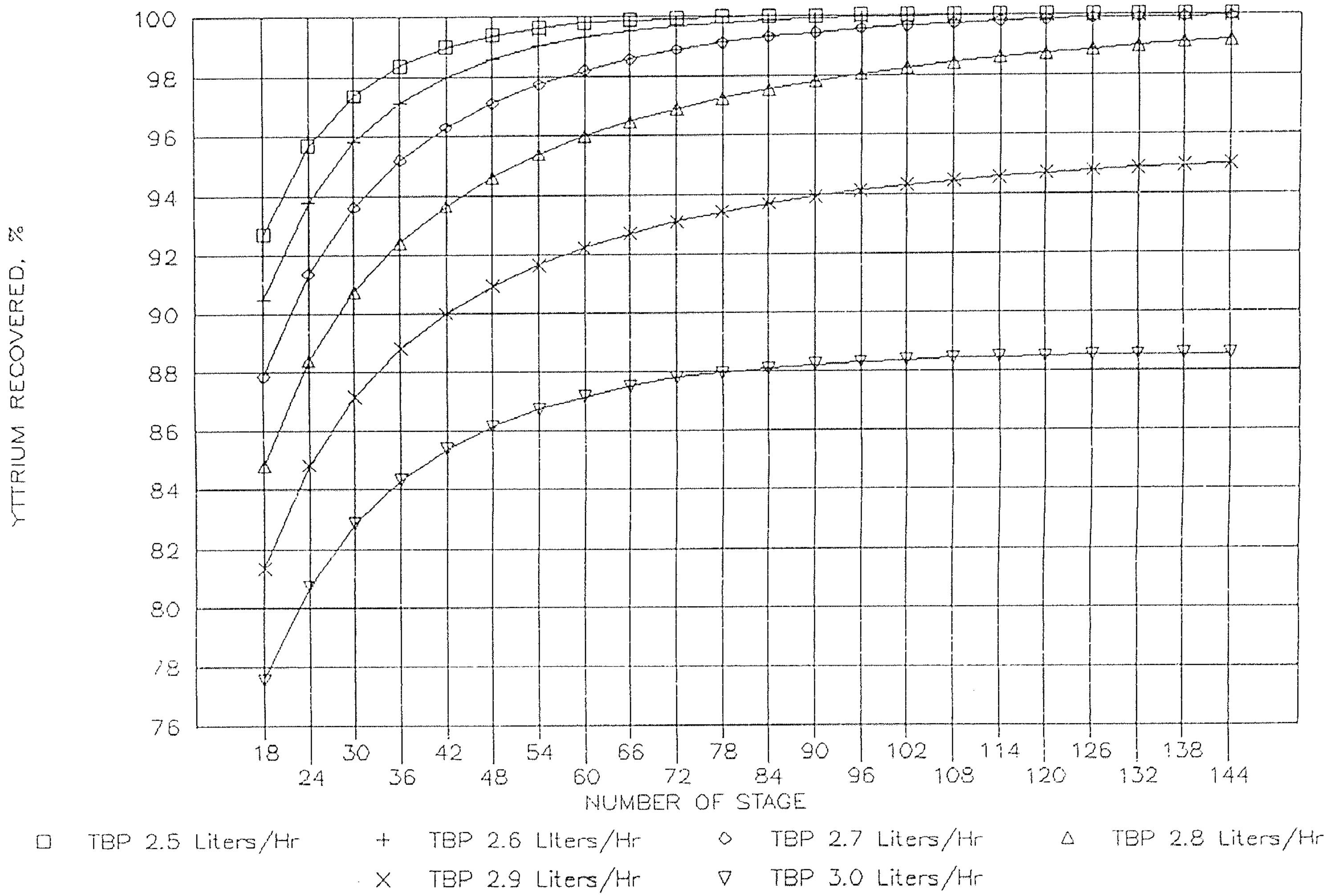

Figure 7.4 The Effect of Number of Stages on Yttrium Purification, Yttrium Recovered %, HNO_3 6.4 N.

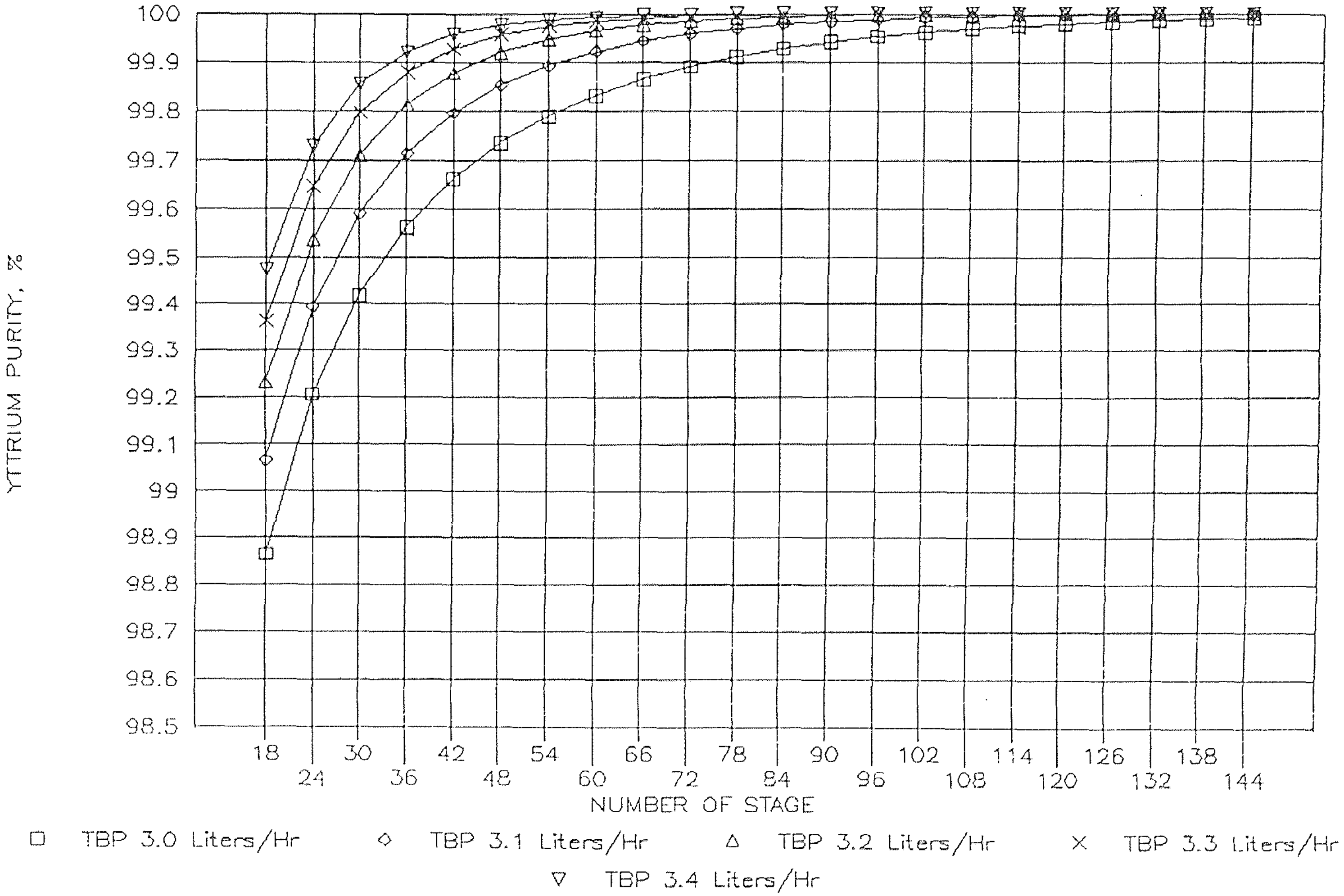

Figure 7.6 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO_3 6.2 N.

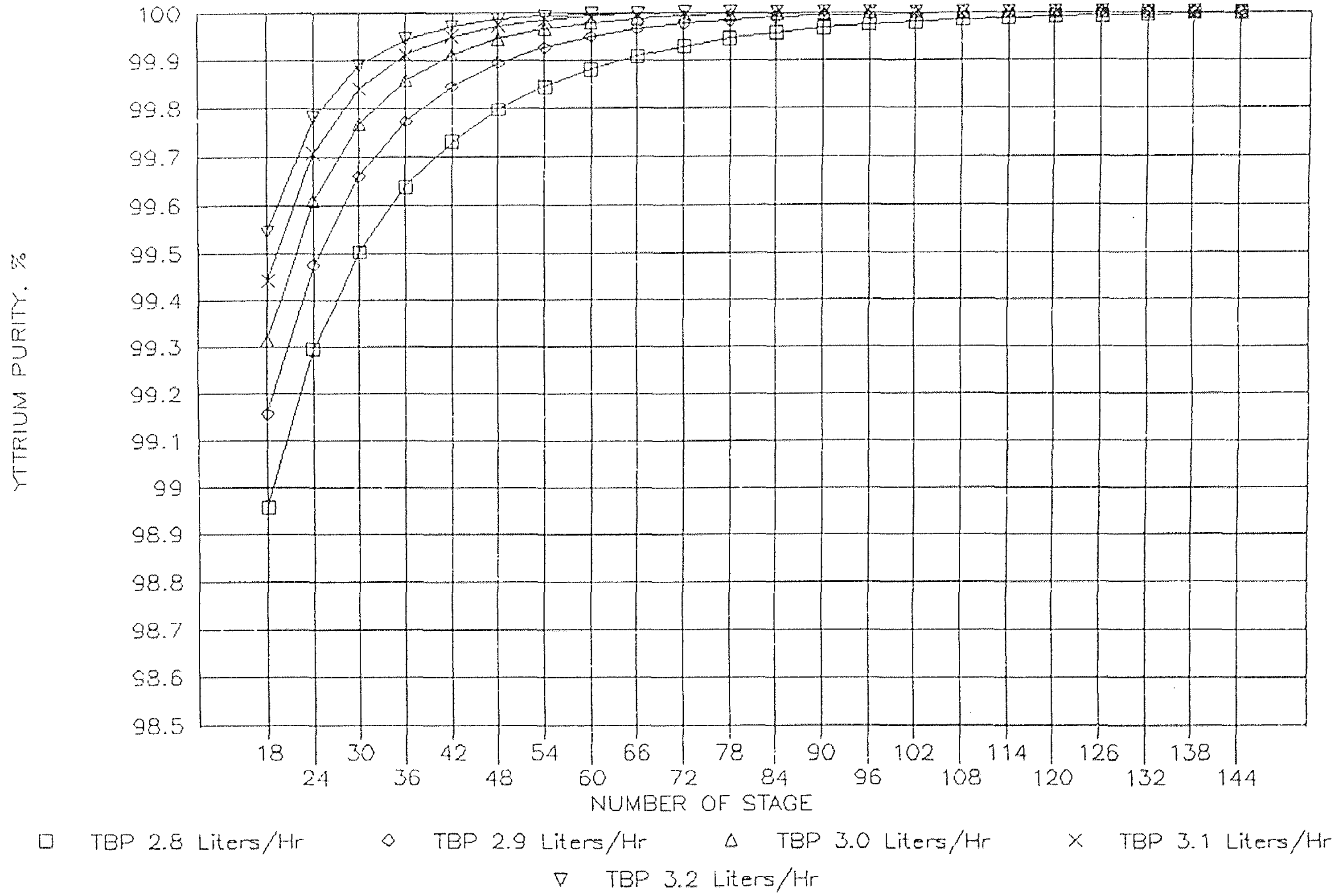

Figure 7.7 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO_3 6.3 N.

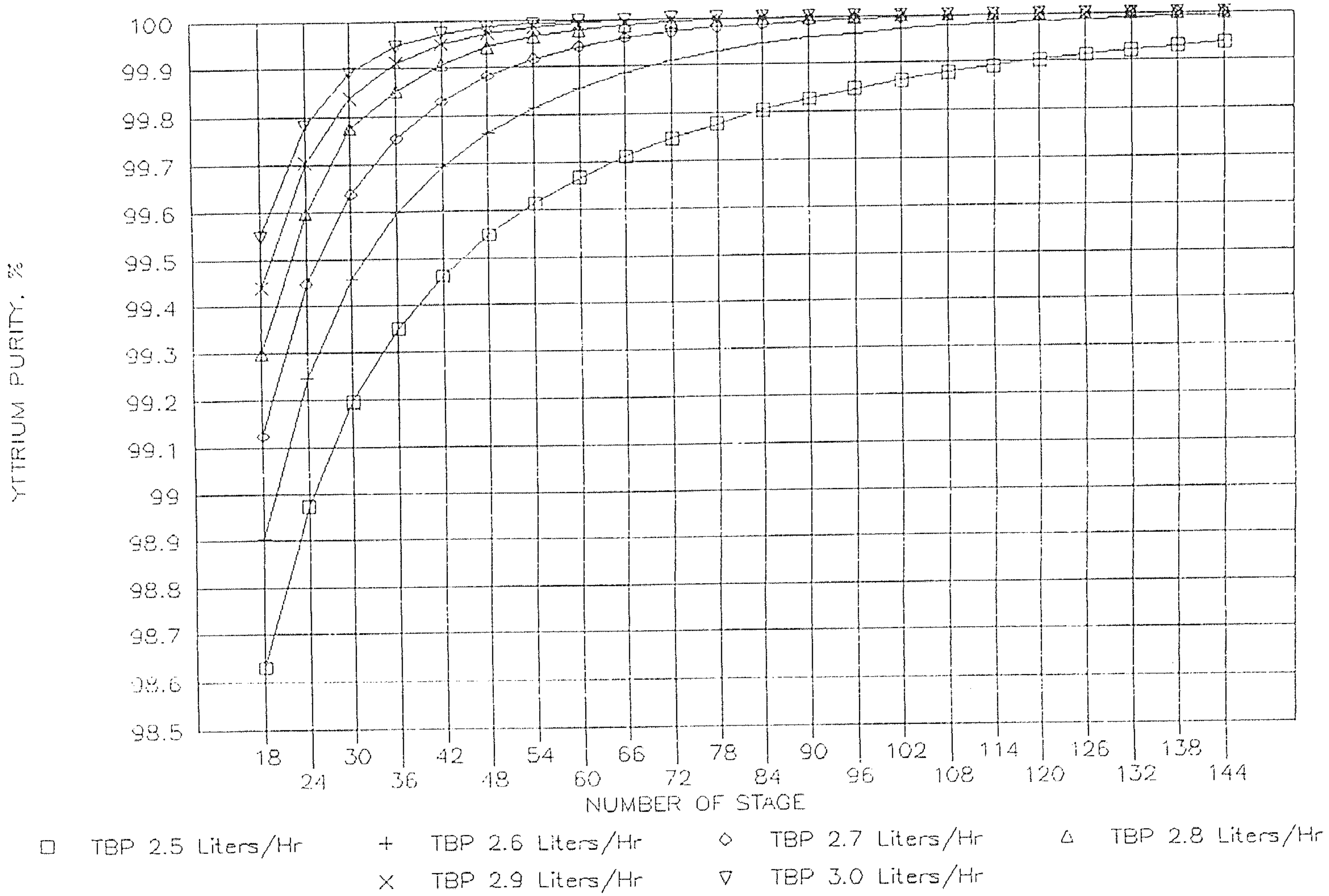

Figure 7.8 The Effect of Number of Stages on Yttrium Purification, Yttrium Purity %, HNO_3 6.4 N.

APPENDIX C

Computer Program for Evaluation of Model Parameters

```
C     MAIN PROGRAM
C
C     DECLARATION OF VARIABLES, DOUBLE PRECISION
C
      INTEGER  LDFJAC, M, N, NTEST, NPRAM, NOUT
      PARAMETER (LDFJAC=9, M=9, N=9, NTEST=12, NPARM=8)
      INTEGER  IPARAM(7), ITP
C
      DOUBLE PRECISION FJAC(LDFJAC,N), FSCALE(M), FVEC(M), HOUSTON,
     &            RPARAM(7), X(N), XGUESS(N), XLB(N), XS(N), XUB(N)
      DOUBLE PRECISION THETA, TABLE, OTHETA, STHETA, AF
      DOUBLE PRECISION XDATA, YDATA, GA, TBP, HNO3, RRE, EA
C
      DIMENSION XDATA(NTEST), YDATA(NTEST), AF(0:3), EA(0:5)
      DIMENSION TABLE(NTEST,14), GA(0:5), THETA(NPARM), OTHETA(NPARM)
C
      COMMON/PARAM1/ TBP, HNO3, RRE, GA
      COMMON/PARAM2/ THETA
      COMMON/PARAM3/ TABLE
      COMMON/PARAM4/ AF, EA
C
      EXTERNAL  DBCLSF, UMACH, HOUSTON, DOVER, DU4LSF
C
C     FOLLOWING ARE INITIAL DATA AND DATA ESTIMATION
C
C     INITIAL TBP, HNO3 AND RARE EARTH CONCENTRATIONS
      TBP  = 3.66
      HNO3 = 0.5
      RRE  = 0.01
C
C     INITIAL ESTIMATED BETA1, BETA2, BETA3 AND KE
      THETA(1) = 0.0000
      THETA(2) = 12.500
      THETA(3) = 0.0000
      THETA(4) = 0.003800
      THETA(5) = 16.775
      THETA(6) = 0.7250000
      THETA(7) = 0.000002616
      THETA(8) = 8.0000
C
C     HNO3 DEGREE OF IONIZATION CURVE FIT PARAMETERS
      AF(0) = 1.0006204
      AF(1) = -0.020407
      AF(2) = -0.004496
      AF(3) = 0.0001546
C
C     HNO3 IN ORGANIC PHASE EQUALIBRIUM CURVE FIT PARAMETERS
      GA(0) = -0.07272
      GA(1) =  1.062423
      GA(2) = -0.173784
      GA(3) =  0.0186665
      GA(4) = -0.001062
      GA(5) =  0.0000261
C
C     TBP IN ORGANIC PHASE EQUILIBRIUM CURVE FIT PARAMETERS
      EA(0) =  3.428093
      EA(1) = -0.13173
      EA(2) =  0.028538
      EA(3) = -0.003824
      EA(4) =  0.0002462
```

```
      EA(5) = -0.000006359
C
C     EXPERIMENTAL KD DATA TO BE FITTED INTO MODEL
C
C     THULIUM
      DATA XDATA/0.58, 1.28, 2.43, 2.72, 3.70, 4.74, 7.38, 8.30, 9.22,
     &      10.4, 11.1, 14.0/
      DATA YDATA/0.027, 0.076, 0.17, 0.23, 0.39, 0.65, 2.0, 3.2, 5.4,
     &      10.0, 16.2, 97.00/
C
C
C     THE GUESS RESULTS OF ALL X FOR THE FIRST OBSERVATION
      DATA XGUESS/0.15, 3.50, 0.15, 0.15, 0.15, 0.003, 0.003, 0.98, 1.0/
C
C     ALL THE BOUNDS ARE PROVIDED
      DATA XLB/0.0, 0.0001, 0.0, 0.0001, 0.0, 0.0001, 0.0001, 0., 1.0/
      DATA XUB/1.00, 3.60, 1.00, 6.66, 1.00, 0.010, 0.010, 1.00, 8.0/
C
C     MISCELLANEOUS DATA
      DATA XS/N*1.0E0/, FSCALE/M*1.0E0/, NOUT/6/
C
C     COMPUTE THE LEAST SQUARES FOR ROSENBROCK FUNCTION
      ITP=0
C
      DO 35 J=1, N
         TABLE(1,J+3)=XGUESS(J)
 35   CONTINUE
C
      CALL UMACH (2, NOUT)
C
      DO 500 JK=1, 30
C
      STHETA=0.0
      DO 45 JB=1, NPARM
         STHETA=STHETA+(OTHETA(JB)-THETA(JB))**2
 45   CONTINUE
C
      IF (STHETA.LT.1.0E-6) THEN
          GOTO 600
      ENDIF
C
      DO 55 IJ=1, N
         XGUESS(IJ)=TABLE(1,IJ+3)
 55   CONTINUE
C
      DO 400 I=1, NTEST
C
C     DEFAULT PARAMETER ARE NOT USED
C     ITP=0
      CALL DU4LSF (IPARAM, RPARAM)
      IPARAM(3)=500
      IPARAM(4)=500
      IPARAM(5)=500
C
C     INITIALIZE THE HNO3 CONCENTRATION AND SOLUTION BOUNDS
      HNO3=XDATA(I)
C     XLB(8)=TABLE(I,11)
      XUB(1)=XDATA(I)
      XUB(3)=XDATA(I)
      XUB(5)=XDATA(I)
```

```
      CALL DBCLSF (HOUSTON, M, N, XGUESS, ITP, XLB, XUB, XS, FSCALE,
     &             IPARAM, RPARAM, X, FVEC, FJAC, LDFJAC)
C
      WRITE (NOUT, 2000) IPARAM(3), IPARAM(4), FVEC
 2000 FORMAT(/, ' THE NUMBER OF ITERATION FOR THETA IS ', 5X, I6, /,
     &        ' THE NUMBER OF FUNCTION EVALUATION IS ', 5X, I6, /,
     &        ' THE FUNCTION EVALUATED FOR THETA AT THE SOLUTION IS',
     &         /, 2X,10F9.4)
C
C     FILLING TABLE
C
      TABLE(I,1)=XDATA(I)
      TABLE(I,2)=YDATA(I)
      TABLE(I,3)=(THETA(4)*(X(1)*X(2))**3)*(THETA(5)+
     &             THETA(6)*X(3)**(1.9068)+THETA(7)*X(3)**THETA(8))/
     &             (1.0+THETA(1)*X(1)+THETA(2)*X(1)**2+THETA(3)*X(1)**3)

      DO 200 J=1, N
      XGUESS(J)=X(J)
      TABLE(I,J+3)=X(J)
200   CONTINUE
      TABLE(I,13)=(THETA(4)*(X(1)*X(2))**3)/(1.0+THETA(1)*X(1)+THETA(2)*
     &             X(1)**2+THETA(3)*X(1)**3)
      TABLE(I,14)=(THETA(5)+
     &             THETA(6)*X(3)**(1.9068)+THETA(7)*X(3)**THETA(8))
 400  CONTINUE
C
      DO 75 JB=1, NPARM
         OTHETA(JB)=THETA(JB)
 75   CONTINUE
C
      CALL OUTPUT (NPARM, TABLE, N, NTEST, NOUT, THETA, JK)
C
      CALL R2D2 (ITP, IPARAM, RPARAM, THETA)
C
 500  CONTINUE
 600  END
C
      SUBROUTINE HOUSTON (M, N, X, F)
C
      INTEGER  M, N
      PARAMETER(NPARM=8)
      DOUBLE PRECISION X(N), F(M)
      DOUBLE PRECISION TBP, HNO3, RRE, GA, AF, THETA, EA
C
      DIMENSION AF(0:3), THETA(NPARM), GA(0:5), EA(0:5)
C
      COMMON/PARAM1/ TBP, HNO3, RRE, GA
      COMMON/PARAM2/ THETA
      COMMON/PARAM4/ AF, EA
C
C     TEN EQUATIONS
C
      F(1)  = X(8)-AF(0)-AF(1)*X(3)-AF(2)*X(3)**2-AF(3)*X(3)**3
      F(2)  = X(1)-X(3)*X(8)
      F(3)  = X(4)-GA(0)-GA(1)*X(3)-GA(2)*X(3)**2-GA(3)*X(3)**3-
     &        GA(4)*X(3)**4-GA(5)*X(3)**5
      F(4)  = X(6)-THETA(4)*X(7)*(X(1)*X(2))**3
      F(5)  = HNO3-X(5)-X(3)+X(3)*X(8)-X(4)-RRE/3.0
      F(6)  = RRE-X(7)-THETA(1)*X(1)*X(7)-THETA(2)*X(7)*X(1)**2-
```

```
     &       THETA(3)*X(7)*X(1)**3-X(6)
      F(7) = HNO3-X(3)-X(4)-3.0*X(6)-THETA(1)*X(1)*X(7)-THETA(2)*
     &       X(7)*X(1)**2-THETA(3)*X(7)*X(1)**3
      F(8) = TBP-3.0*X(6)-X(2)-X(4)/X(9)
      F(9) = X(2)-EA(0)-EA(1)*X(3)-EA(2)*X(3)**2-EA(3)*X(3)**3-
     &       EA(4)*X(3)**4-EA(5)*X(3)**5
C
      RETURN
      END
C
C
      SUBROUTINE R2D2 (ITP, IPARAM, RPARAM, THETA)
C
      INTEGER  LDFJAC, M, N, ITP, IPARAM(7), NTEST, NPARM, NOUT
      PARAMETER (LDFJAC=12, M=12, N=8)
      DOUBLE PRECISION FJAC(LDFJAC,N), FSCALE(M), FVEC(M), DOVER,
     &           RPARAM(7), X(N), XGUESS(N), XLB(N), XS(N), XUB(N)
      DOUBLE PRECISION  THETA, TABLE
C
      DIMENSION THETA(N), TABLE(M,14)
      COMMON/PARAM3/ TABLE
C
      EXTERNAL  DBCLSF, DOVER, DU4LSF
C
C     FOLLOWING ARE INITIAL DATA AND DATA ESTIMATION
C
C     THE ESTIMATED THETA AND BOUNDS
      DO 100 I=1, N
         XGUESS(I)=THETA(I)
 100  CONTINUE
      WRITE (NOUT, 1010) (XGUESS(I), I=1,N)
 1010 FORMAT (/,' THE  GUESSED  THETA  ARE  = ', 8E12.5)
      DATA XS/N*1.0E0/, FSCALE/M*1.0E0/, NOUT/6/
      DATA XLB/0.7079, 12.5, 0.00, 0.00, -999., -999., -999., -999./
      DATA XUB/999., 99.00, 0.0, 2.50, 999., 999., 999., 999./
C
      ITP=0
      CALL DU4LSF (IPARAM, RPARAM)
      IPARAM(3)=500
      IPARAM(4)=500
      IPARAM(5)=500
C
C
      CALL DBCLSF (DOVER, M, N, XGUESS, ITP, XLB, XUB, XS, FSCALE,
     &           IPARAM, RPARAM, X, FVEC, FJAC, LDFJAC)
C
      WRITE (NOUT, 1111) (X(J), J=1,N)
 1111 FORMAT (' THE CALC THETA AFTER R2D2 = ',8E12.5)
      DO 300 J=1, N
         THETA(J)=X(J)
 300  CONTINUE
C
      WRITE (NOUT, 3000) IPARAM(3), IPARAM(4), FVEC
 3000 FORMAT(/, ' THE NUMBER OF ITERATION FOR THETA IS ', 5X, I6, /,
     &       ' THE NUMBER OF FUNCTION EVALUATION IS ', 5X, I6, /,
     &       ' THE FUNCTION EVALUATED FOR THETA AT THE SOLUTION IS',
     &        /, 2X,14F9.4, /, 2X, 14F9.4)
      RETURN
      END
C
```

```
C
C
      SUBROUTINE DOVER (M, N, X, F)
C
      INTEGER  M, N
      PARAMETER (NTEST=12, NPARM=8)
      DOUBLE PRECISION  F(M), X(N)
      DOUBLE PRECISION  TABLE
C
      DIMENSION TABLE(NTEST,14)
      COMMON/PARAM3/ TABLE
C
      DO 300 J=1, M
      F(J)=TABLE(J,2)-
     &     (X(4)*(TABLE(J,4)*TABLE(J,5))**3)*
     &     (X(5)+X(6)*TABLE(J,6)**(1.9068)+X(7)*TABLE(J,6)**X(8))/
     &     (1.0+X(1)*TABLE(J,4)+X(2)*TABLE(J,4)**2+
     &      X(3)*TABLE(J,4)**3)
 300  CONTINUE
C
      RETURN
      END
C
C
      SUBROUTINE OUTPUT (NPARM, TABLE, N, NTEST, NOUT, THETA, JK)
C
      INTEGER  N, NTEST, NOUT, JK, NPARM
      DIMENSION TABLE(NTEST,14), THETA(NPARM)
      DOUBLE PRECISION TABLE, THETA
C
C                     PRINT RESULTS
C
      WRITE (NOUT, 4000)  JK
C
      WRITE (NOUT, 5000) THETA
C
      WRITE (NOUT, 6000)
C
      DO 103 I=1, NTEST
      WRITE (NOUT, 7000) I, (TABLE(I,J), J=1, 14)
 103  CONTINUE
C
 4000 FORMAT (/, '   NUMBER OF ITERATIONS FOR THETA = ', I5)
 5000 FORMAT (/,'   THE THETAE ', 2X, E12.5, 2X, E12.5, 2X, E12.5,
     &       2X, E12.5,2X,E12.5,2X,E12.5,2X,E12.5,2X,E12.5)
 6000 FORMAT (/, 2X, 'RUN', 2X, '(HNO3)AI', 3X, 'KD EXP',2X, 'KD CALC',
     &       2X, '(NO3-1)A', 2X, '(TBP)O',
     &       2X, '(HNO3)AT', 2X, '(HNO3)O', 2X, '(H+1)A',
     &       3X, '( M )O', 3X, '(M+3)A', 2X, 'DEG ION',
     &       1X, 'NO (HNO3)O', 2X, 'KD1', 3X, 'KD2')
C
 7000 FORMAT (2X, I3, 2X, F6.2, 2X, 13F9.4)
C
      RETURN
      END
```

APPENDIX D

Computer Program for Liquid-Liquid Extraction Computation

```
C
C------MAIN PROGRAM
C-----MULTICOMPOINENT MULSTAGE COUNTER-CURRENT LIQUID-LIQUID EXTRACTION
C------KENNETH Y. CHAN   JULY 12, 1992
C
      INTEGER PHASE
      CHARACTER*1 PAGEJC,SNGLSP,DUBLSP
      CHARACTER*16 COMP(20)
      DOUBLE PRECISION XFEED(20),VOLD(20),F(100),L(100),B(6,20)
      DOUBLE PRECISION W(100),U(100),V(100),A(100,101),XFLOW
      DOUBLE PRECISION X(20,100),Y(20,100),XSUM(100),YSUM(100)
      DOUBLE PRECISION XF(20,100),AK(20,100),KCONST(8,20)
      DOUBLE PRECISION STD,TAL,TOL,DIFF,VRATE,RATE,SUM,SUMMF
      DOUBLE PRECISION HNO3(100),MW(20),TXFLOW,TFHNO3
      DOUBLE PRECISION C(2,20),REFTOT,ETOTAL,RTOTAL
      DIMENSION JP(20),PH(2)
      COMMON/BK1/JS,F,W,U,V
      COMMON/BK2/X,Y,XSUM,YSUM
      COMMON/BK3/XF,L,AK
      COMMON/BK4/KCONST,HNO3
      COMMON/BK5/A
      OPEN(UNIT=5,FILE='GENLLE.INP',STATUS='OLD')
      OPEN(UNIT=6,FILE='GENLLE.OUT',STATUS='NEW')
C
      DATA PAGEJC,SNGLSP,BUBLSP/'1',' ','0'/
      DATA PH(1),PH(2)/'ORG','AQU'/
C
C     ASSIGN BASIC COMPONENT NAMES, MOLECULAR WEIGHTS AND
C     PARAMETERS FOR EQUILIBRIUM CONSTANT CORRELATIONS
C
      DATA (COMP(I),I=1,3)/'TBP ','HNO3','H2O '/
      DATA (MW(I),I=1,3)/266.32,63.0,18.0/
      DATA (KCONST(I,1),I=1,8)/.99999999E26,.0,.0,.0,.0,.0,.0,.0/
      DATA (KCONST(I,2),I=1,8)/-25.54334,12.11596,-10.24788,26.14166,
     1                         -5.342299,.0,.0,.0/
      DATA (KCONST(I,3),I=1,8)/.5196597,-4.468081,19.72675,-32.13729,
     1                         19.22704,.0,.0,.0/
C
C     INPUT NUMBER OF RARE EARTH COMPONENTS FOR SEPARATION AND
C     MAXIMUM NUMBER OF COLUMN ITERATIONS AND COLUMN ITERATION
C     CONVERGENCE CRITERION CONSTANT
C
      READ (5,*) NRE, NCI, TAL
      IC = NRE + 3
      IF (IC .LT. 3 .OR. IC .GT. 20) THEN
         WRITE (6,*) 'NUMBER OF COMPONENTS ARE OUT OF PROGRAM LIMITS'
         GO TO 190
      END IF
C
C     INPUT NAME OF RARE EARTH COMPONENTS
C
      READ (5,*) (COMP(I),I=4,IC)
C
C     INPUT MOLECULAR WEIGHT OF RARE EARTH COMPONENTS
C
      READ (5,*) (MW(I),I=4,IC)
C
C     INPUT PARAMETERS FOR RARE EARTH DISTRIBUTION COEFFICIENT MODELS
C
      DO 13 J = 4, IC
         READ (5,*) (KCONST(I,J),I=1,8)
   13 CONTINUE
C
```

```
C     INPUT CASE NUMBER, NUMBER OF STAGES, NUMBER OF FEEDS,
C     NUMBER OF ORGANIC SIDEDRAWS, NUMBER OF AQUEOUS SIDEDRAWS,
C     AND FREQUENCY OF PRINTOUT FOR RESULTS OF COLUMN ITERATION
C
   15 READ (5,*) NC, JS, NOF, NOVS, NOLS, KP
      IF (KP .EQ. 0) THEN
         KP=15
      END IF
      IF (JS .LE. 2 .OR. JS .GT. 100) THEN
         WRITE (6,*)  'NUMBER OF STAGES ARE OUT OF PROGRAM LIMITS'
         GO TO 190
      END IF
C
C     ZERO OUT CERTAIN ARRAYS BEFORE STARTING A CASE
      DO 22 J = 1, 100
         DO 20 I = 1, 20
            AK(I,J)=0.0
            XF(I,J)=0.0
            X(I,J)=0.0
            Y(I,J)=0.0
   20    CONTINUE
         HNO3(J)=0.0
         F(J)=0.0
         V(J)=0.0
         L(J)=0.0
         W(J)=0.0
         U(J)=0.0
   22 CONTINUE
      TOL = TAL* JS
      WRITE (6,219) PAGEJC
  219 FORMAT (A)
      WRITE (6,219) DUBLSP
      WRITE (6,*) 'CASE NUMBER                  ', NC
      WRITE (6,219) SNGLSP
      WRITE (6,*) 'NO. OF CHEMICAL COMPONENTS = ', IC
      WRITE (6,219) SNGLSP
      WRITE (6,*) 'NO. OF THOERETICAL STAGES  = ', JS
      WRITE (6,219) SNGLSP
      WRITE (6,*) 'NO. OF FEED STREAMS        = ', NOF
      WRITE (6,219) SNGLSP
      WRITE (6,*) 'NO. OF ORGANIC SIDEDRAWS   = ', NOVS
      WRITE (6,219) SNGLSP
      WRITE (6,*) 'NO. OF AQUEOUS SIDEDRAWS   = ', NOLS
      WRITE (6,219) DUBLSP
      WRITE (6,240) (JK, COMP(JK),MW(JK), JK=1,IC)
  240 FORMAT (/T10,'COMPONENT NUMBER',T30,'COMPONENT NAMES',T50,
     1         'MOLECULAR WEIGHTS'//(T15,I5,T35,A15,T55,F12.6)/)
      WRITE (6,245) 'FEED AND SIDEDRAWS SPECIFICATIONS'
  245 FORMAT (A34)
      WRITE (6,219) DUBLSP
      WRITE (6,270) 'FLOW RATE', 'PHASE'
  270 FORMAT (///T23,A9,T38,A5)
      WRITE (6,271) 'STAGE', '(KGMOLES/HR)', 'CONDITION',
     1      'COMPONENT MOLE FRACTIONS FOR COMPONENTS 1 TO ', IC, 'FEEDS'
  271 FORMAT (/T15,A5,T22,A12,T36,A9,T63,A45,I3//T5,A5/)
      TXFLOW = 0.0
      TFHNO3 = 0.0
      DO 35 L1 = 1, NOF
         READ (5,*) JF, PHASE,XFLOW
         READ (5,*) (XFEED(I), I = 1, IC)
         IF (PHASE .EQ. 1) THEN
            WPHASE = PH(1)
         ELSE
```

```
            WPHASE = PH(2)
         END IF
         SUMMF = 0.0
         DO 25 M = 1, IC
            SUMMF = SUMMF + XFEED(M)
   25    CONTINUE
         IF (SUMMF .LT. 0.9999 .OR. SUMMF .GT. 1.0001) THEN
            DO 26 M = 1, IC
               XFEED(M)=XFEED(M)/SUMMF
   26       CONTINUE
            WRITE (6,219) DUBLSP
            WRITE (6,*) 'FEED MOLE FRACTIONS FOR STAGE', JF
            WRITE (6,*) 'DO NOT SUM TO 1.000. PROBLEM FIXED'
         END IF
         WRITE (6,285) JF, XFLOW, WPHASE, (XFEED(L2), L2 = 1, IC)
  285    FORMAT (/14X,I5,F15.8,4X,A4,8X,5F14.10/3((50X,5F14.10)/))
         F(JF) = XFLOW
         JP(JF) = PHASE
         IF (PHASE .EQ. 2) THEN
            TXFLOW = TXFLOW + XFLOW
            TFHNO3 = TFHNO3 + XFLOW*XFEED(2)
         END IF
         DO 30 L2 = 1, IC
            XF(L2,JF) = XFEED(L2)
   30    CONTINUE
   35 CONTINUE
C
C     COMPUTE INITIAL HNO3 MOLE FRACTIONS IN AQUEOUS PHASE
C
      DO 36 J = 1, JS
         X(2,J) = TFHNO3/TXFLOW
   36 CONTINUE
      KKK = 0
      IF (NOVS .EQ. 0) THEN
         GO TO 45
      ELSE
         WPHASE = PH(1)
         WRITE (6,*) '   SIDEDRAWS'
         KKK = 1
         DO 40 L3 = 1, NOVS
            READ (5,*) JSV, VRATE
            WRITE (6,295) JSV, VRATE, WPHASE
  295       FORMAT (/14X,I5,F15.8,4X,A4)
            IF (JSV .LT. 2 .OR. JSV .GT. (JS-1)) THEN
               GO TO 190
            ELSE
               W(JSV) = VRATE
            END IF
   40    CONTINUE
      END IF
   45 IF (NOLS .EQ. 0) THEN
         GO TO 55
      ELSE
         WPHASE = PH(2)
         IF (KKK .EQ. 0) THEN
            WRITE (6,*) '   SIDEDRAWS'
         END IF
         DO 50 L4 = 1, NOLS
            READ (5,*) JSL, RATE
            WRITE (6,295) JSL, RATE, WPHASE
            IF (JSL .LT. 2 .OR. JSL .GT. (JS-1)) THEN
               GO TO 190
            ELSE
```

```
               U(JSL) = RATE
            END IF
   50    CONTINUE
      END IF
C
C     COMPUTE INITIAL ORGANIC RATE PROFILES - INITIALIZE TEAR VARIABLES
C
   55 JK = JS - 1
      V(JS) = F(JS) - W(JS)
      DO 60 J = JK, 1, -1
         IF (JP(J) .EQ. 2) THEN
            V(J) = V(J+1) - W(J)
         ELSE
            V(J) = V(J+1) + F(J) - W(J)
         END IF
   60 CONTINUE
      WRITE (6,325) 'INTERMIDIATE RESULTS WILL BE PRINTED OUT EVERY',
     1              KP,'COLUMN ITERATIONS'
  325 FORMAT (//A48,I5,2X,A17/)
C
C     COMPUTE INITIAL AQUEOUS RATE PROFILES
C
      JL1 = JS - 1
      SUM = 0.0
      DO 70 I = 1, JL1
         SUM = SUM + F(I) - W(I) - U(I)
         L(I) = V(I+1) + SUM - V(1)
   70 CONTINUE
      L(JS) = SUM + F(JS) - W(JS) - U(JS) - V(1)
      K1 = 0
      K2 = 0
   75 K1 = K1 + 1
      K2 = K2 + 1
      DO 78 J = 1, JS
         DO 77 I = 1, IC
            IF (I .LE. 3) THEN
               CALL BASEKV(J)
            ELSE
               CALL EQUILK(I,J)
            END IF
   77    CONTINUE
         VOLD(J) = V(J)
   78 CONTINUE
C
C     COMPUTE MATRIX COEFFICIENTS FOR AQUEOUS MOLE FRACTION
C
      DO 80 I = 1, IC
         CALL SETUPA (I)
C
C     SOLVE MATRIX FOR AQUEOUS MOLE FRACTIONS
C
         CALL THOMAS(I)
   80 CONTINUE
C
C     COMPUTE ORGANIC MOLE FRACTIONS, AND NEW ORGANIC RATE PROFILES
C
      DO 95 JA = 1, JS
         XSUM(JA) = 0.0
         YSUM(JA) = 0.0
         DO 85 I = 1, IC
            IF (X(I,JA) .GT. 1.0) THEN
               X(I,JA) = (X(I,JA) + 1.0) / 2.0
            END IF
```

```
            IF (X(I,JA) .LT. 0.0) THEN
               X(I,JA) = X(I,JA) / 2.0
            END IF
            XSUM(JA) = XSUM(JA) + X(I,JA)
   85    CONTINUE
         DO 90 I = 1, IC
            X(I,JA) = X(I,JA) / XSUM(JA)
            Y(I,JA) = X(I,JA) * AK(I,JA)
            YSUM(JA) = YSUM(JA) + Y(I,JA)
   90    CONTINUE
         V(JA) = V(JA) * YSUM(JA)
   95 CONTINUE
C
C     COMPUTE NEW AQUEOUS RATE PROFILE
C
      JL2 = JS - 1
      SUM = 0.0
      DO 100 I = 1, JL2
         SUM = SUM + F(I) - W(I) -U(I)
         L(I) = V(I+1) + SUM - V(1)
  100 CONTINUE
      L(JS) = SUM + F(JS) - W(JS) - U(JS) -V(1)
      DO 110 J = 1, JS
         IF (V(J) .LT. 0.0) THEN
            WRITE (6,445) 'COMPUTED ORGANIC RATE OF', V(J), 'FOR STAGE',
     1                    J, 'OF COLUMN ITERATION', K1, 'IS NEGATIVE'
  445       FORMAT (//T20,A24,F15.8,T58,A9,I4,T73,A19,I4,T98,A8/)
            WRITE (6,*)
            WRITE (6,*) 'THE FEED OR SIDESTREAM SPECIFICATIONS'
            WRITE (6,*) 'MAY BE IMPROPER. CASE TERMINATED'
            WRITE (6,*) 'SHOULD REPEAT RUN WITH REVISED SPECIFICATIONS'
            GO TO 15
         END IF
         IF (L(J) .LT. 0.0) THEN
            WRITE (6,455) 'COMPUTED AQUEOUS RATE OF', L(J), 'FOR STAGE',
     1                    J, 'OF COLUMN ITERATION', K1, 'IS NEGATIVE'
  455       FORMAT (//T20,A24,F15.8,T58,A9,I4,T73,A19,I4,T98,A8/)
            WRITE (6,*)
            WRITE (6,*) 'THE FEED OR SIDESTREAM SPECIFICATIONS'
            WRITE (6,*) 'MAY BE IMPROPER. CASE TERMINATED'
            WRITE (6,*) 'SHOULD REPEAT RUN WITH REVISED SPECIFICATIONS'
            GO TO 15
         END IF
  110 CONTINUE
      IF (K2 .NE. KP .AND. K1 .NE. NCI) THEN
         GO TO 130
      ELSE
         WRITE (6,*)
         WRITE (6,*) 'INTERMEDIATE RESULTS FOR ITERATION ', K1
         WRITE (6,330) 'ORGANIC RATE', 'AQUEOUS RATE',
     1         'AQUEOUS, FOLLOWED BY ORGANIC MOLE FRACTION',
     1         'ORGANIC MOLE'
  330    FORMAT (///T13,A12,T29,A12,T64,A43,T119,A12)
         WRITE (6,331) 'STAGE', '(KGMOLES/HR)', '(KGMOLES/HR)',
     1                  'FOR COMPONENTS 1 TO ', IC, 'FRACTION SUM'
  331    FORMAT (/T5,A5,T13,A12,T29,A12,T74,A20,I3,T119,A12/)
         K2 = 0
         DO 125 J = 1, JS
            WRITE (6,335) J, L(J),(X(I,J), I = 1, IC)
  335       FORMAT (/4X,I4,15X,F15.8,12X,5F14.10/3((50X,5F14.10)/))
            WRITE (6,345) V(J),(Y(I,J), I = 1, IC)
  345       FORMAT (/8X,F15.8,27X,5F14.10/3((50X,5F14.10)/))
            WRITE (6,340) YSUM(J)
```

```
  340       FORMAT (/116X,F14.10/)
  125    CONTINUE
      END IF
C
C     CONVERGENCE TEST
C
  130 STD = 0.0
      DO 135 J = 1, JS
         DIFF = V(J) - VOLD(J)
         STD = STD + (DIFF / V(J))**2
  135 CONTINUE
      IF (STD .GT. TOL .AND. K1 .LE. NCI) THEN
         WRITE (6,355) 'AFTER ITERATION',K1,
     1                 'CALCULATIONS ARE NOT CONVERGED'
  355    FORMAT (//A16,I5,2X,A31/)
         WRITE (6,*) 'COLUMN ITERATION CONVERGENCE FACTOR IS', STD
         WRITE (6,*) 'WHICH IS GREATER THAN TOLERANCE OF    ', TOL
         GO TO 75
      ELSE IF (STD .LE. TOL .AND. K1 .LE. NCI) THEN
         GO TO 140
      ELSE
         WRITE (6,365) 'CALCULATION ARE NOT CONVERGED AFTER THE ',
     1    'ITERATIONS EXCEED THE MAXIMUM NUMBER', NCI
  365 FORMAT (//A40,A36,I5)
         WRITE (6,*) 'THE UNCONVERGED RESULTS ARE PRINTED AS FOLLOW'
         WRITE (6,*) 'REPEAT CASE WITH A LARGER VALUE OF NCI'
         GO TO 145
      END IF
  140 WRITE (6,360) 'AFTER ITERATION', K1,
     1              'CALCULATIONS ARE CONVERGED'
  360 FORMAT (//A16,I5,2X,A26/)
      WRITE (6,*) 'COLUMN ITERATION CONVERGENCE FACTOR IS', STD
      WRITE (6,*) 'WHICH IS LESS THAN TOLERANCE OF       ', TOL
      WRITE (6,*)
      WRITE (6,*) 'FINAL DETAILED RESULTS ARE AS FOLLOW'
      WRITE (6,219) PAGEJC
  145 WRITE (6,361) DUBLSP,'FINAL RESULTS OF PRODUCT STREAMS'
  361 FORMAT (A,A33)
      WRITE (6,370) 'FROM', 'PHASE', 'FLOW RATE',
     1              'COMPONENT MOLE FRACTIONS'
  370 FORMAT (//T16,A4,T24,A5,T38,A9,T70,A25)
      WRITE (6,371) 'STREAM', 'STAGE', 'CONDITION', '(KGMOLES/HR)',
     1              'FOR COMPONENTS 1 TO ', IC
  371 FORMAT (/T5,A6,T15,A5,T23,A9,T36,A12,T71,A20,I4)
      WRITE (6,375) PH(1), V(1), (Y(K,1), K=1, IC)
  375 FORMAT (/5X,'EXTRACT',5X,2H 1,5X,A4,3X,F15.8,4X,5F14.10/
     1       3((50X,5F14.10)/))
      JSS = JS - 1
      IF (NOVS .EQ. 0) THEN
         GO TO 155
      ELSE
         DO 150 I = 2, JSS
            IF (W(I) .LT. .00001) THEN
               GO TO 150
            ELSE
               WRITE (6,380) I, PH(1), W(I), (Y(K,I), K=1, IC)
            END IF
  150    CONTINUE
      END IF
  155 IF (NOLS .EQ. 0) THEN
         GO TO 165
      ELSE
         DO 160 I = 2, JSS
```

```
            IF (U(I) .LT. .00001) THEN
               GO TO 160
            ELSE
               WRITE (6,380) I, PH(2), U(I), (X(K,I), K=1, IC)
  380          FORMAT (/5X,'SIDEDRAW',T17,I3,5X,A4,3X,F15.8,4X,
     1                  5F14.10/3((50X,5F14.10)/))
            END IF
  160    CONTINUE
      END IF
  165 WRITE (6,385) JS, PH(2), L(JS), (X(K,JS), K=1, IC)
  385 FORMAT (/5X,'RAFFINATE',2X,I3,5X,A4,3X,F15.8,4X,5F14.10/
     1       3((50X,5F14.10)/))
      WRITE (6,219) PAGEJC
      WRITE (6,219) DUBLSP
  175 WRITE (6,390) 'CONCENTRATION PROFILES AND',
     1              'DISTRIBUTION COEFFICIENTS'
  390 FORMAT (A27,1X,A25)
      WRITE (6,395) 'PHASE','ORGANIC RATE', 'AQUEOUS RATE',
     1              'COMPONENT MOLE FRACTIONS'
  395 FORMAT (//T11,A5,T22,A12,T38,A12,T70,A25)
      WRITE (6,396) 'STAGE', 'CONDITION','(KGMOLES/HR)', '(KGMOLES/HR)',
     1              'FOR COMPONENTS 1 TO ', IC
  396 FORMAT (/T2,A5,T9,A9,T22,A12,T38,A12,T71,A20,I4)
      DO 185 I = 1, JS
         WRITE (6,400) I, PH(1), V(I), (Y(K,I), K=1, IC)
  400    FORMAT (//2X,I4,5X,A4,2X,F15.8,18X,5F14.10/3((50X,5F14.10)/))
  180    WRITE (6,405) I, PH(2), L(I), (X(K,I), K=1, IC)
  405    FORMAT (/2X,I4,5X,A4,16X,F15.8,4X,5F14.10/3((50X,5F14.10)/))
         WRITE (6,401) 'HNO3 IN STAGE',I, HNO3(I),'M','KD =',
     1                  (AK(K,I), K=1, IC)
  401    FORMAT (/T10,A13,I5,T30,F8.4,1X,A1,5X,A4,2X,5E14.6/
     1           3((50X,5E14.6)/))
  185 CONTINUE
C
C     PRINT SUMMARY TABLES
C
      WRITE (6,219) PAGEJC
      WRITE (6,490) DUBLSP,' SUMMARY TABLE 1'
  490 FORMAT (A,A16)
      WRITE (6,470) 'COMPONENT','COMPONENT','TOTAL FEED','TOTAL FEED',
     1              'EXTRACT', 'RAFFINATE','% RECOVERY',
     1              '% RECOVERY'
  470 FORMAT (////T2,A10,T15,A9,T35,A10,T51,A10,T69,A7,T84,A9,
     1            T101,A10,T117,A10)
      WRITE (6,475) 'NUMBER','NAME','(KGMOLE/HR)','(KG/HR)',
     1              '(KG/HR)', '(KG/HR)','FROM EXTRACT',
     1              'FROM RAFFINATE'
  475 FORMAT (/T3,A7,T17,A4,T35,A11,T53,A7,T69,A7,T85,A7,
     1         T100,A12,T115,A14)
      DO 215 J=1, 20
         DO 210 I=1, 6
            B(I,J)=0.0
  210    CONTINUE
         DO 211 I=1, 2
            C(I,J)=0.0
  211    CONTINUE
  215 CONTINUE
      DO 205 I=1, IC
         DO 200 J=1, JS
            B(1,I) = B(1,I) + F(J)*XF(I,J)
  200    CONTINUE
         B(2,I) = B(1,I)*MW(I)
         B(3,I) = V(1)*Y(I,1)*MW(I)
```

```
         B(4,I) = L(JS)*X(I,JS)*MW(I)
         B(5,I) = B(3,I)*100.0/B(2,I)
         B(6,I) = B(4,I)*100.0/B(2,I)
         WRITE (6,480) I, COMP(I), (B(J,I), J=1,6)
  205 CONTINUE
  480 FORMAT (/I5,T15,A15,5X,4(E12.6,4X),2(F12.6,4X))
      WRITE (6,219) PAGEJC
      WRITE (6,490) DUBLSP,' SUMMARY TABLE 2'
      WRITE (6,219) DUBLSP
      REFTOT = 0.0
      ETOTAL = 0.0
      RTOTAL = 0.0
      DO 206 I=4,IC
         REFTOT = REFTOT + B(2,I)
         ETOTAL = ETOTAL + B(3,I)
         RTOTAL = RTOTAL + B(4,I)
  206 CONTINUE
      WRITE (6,484) 'TOTAL RARE EARTH IN FEEDS     =',REFTOT,' KG/HR'
      WRITE (6,484) 'TOTAL RARE EARTH IN EXTRACT   =',ETOTAL,' KG/HR'
      WRITE (6,484) 'TOTAL RARE EARTH IN RAFFINATE =',RTOTAL,' KG/HR'
  484 FORMAT (//3X,A31,E14.6,1X,A6)
      WRITE (6,481) 'COMPONENT','COMPONENT','EXTRACT','RAFFINATE'
  481 FORMAT (////T2,A10,T15,A9,T35,A7,T51,A9)
      WRITE (6,482) 'NUMBER','NAME','WT. %','WT. %'
  482 FORMAT (/T3,A7,T17,A4,T36,A5,T53,A5)
      DO 207 I=4,IC
         C(1,I) = B(3,I)*100.0/ETOTAL
         C(2,I) = B(4,I)*100.0/RTOTAL
         WRITE (6,483) I, COMP(I), (C(J,I), J=1,2)
  207 CONTINUE
  483 FORMAT (/I5,T15,A15,2X,2(F12.6,4X))
      GO TO 15
  190 WRITE (6,*) 'DATA INPUT MAY CONTAIN ERROR, CASE TERMINATED'
      STOP
      END
C
C
C
      SUBROUTINE BASEKV(J)
      DOUBLE PRECISION XF(20,100),L(100),AK(20,100),X(20,100)
      DOUBLE PRECISION KCONST(8,20),HNO3(100),NO3,TBP
      COMMON/BK2/X,Y,XSUM,YSUM
      COMMON/BK3/XF,L,AK
      COMMON/BK4/KCONST,HNO3
      AK(1,J)=KCONST(1,1)
      AK(2,J)=KCONST(1,2)+KCONST(2,2)*X(2,J)+KCONST(3,2)*X(2,J)**2+
     1        KCONST(4,2)*X(2,J)**(-.2)+KCONST(5,2)*X(2,J)**(-.4)
      AK(3,J)=KCONST(1,3)+KCONST(2,3)*X(2,J)+KCONST(3,3)*X(2,J)**2+
     1        KCONST(4,3)*X(2,J)**3+KCONST(5,3)*X(2,J)**4
      RETURN
      END
C
C
C
      SUBROUTINE EQUILK(I,J)
      DOUBLE PRECISION XF(20,100),L(100),AK(20,100),X(20,100)
      DOUBLE PRECISION KCONST(8,20),HNO3(100),AT,NO3,TBP
      COMMON/BK2/X,Y,XSUM,YSUM
      COMMON/BK3/XF,L,AK
      COMMON/BK4/KCONST,HNO3
      HNO3(J)=55.62736*X(2,J)-44.62263*X(2,J)**2+72.36273*X(2,J)**3-
     1     358.0529*X(2,J)**4+498.3536*X(2,J)**5
      AT=HNO3(J)
```

```
      NO3 = 1.0006204*AT - 0.020407*AT**2 - 0.004496*AT**3 +
     1       0.0001546*AT**4
      TBP = 3.428093 - 0.13173*AT + 0.028538*AT**2 - 0.003824*AT**3 +
     1      0.0002462*AT**4 - 0.000006359*AT**5
      AK(I,J) = (KCONST(3,I)*(NO3*TBP)**3) * (KCONST(4,I) +
     1        KCONST(5,I)*AT**KCONST(6,I)+KCONST(7,I)*AT**KCONST(8,I))/
     1        (1.0 + KCONST(1,I)*NO3 + KCONST(2,I)*NO3**2)
      RETURN
      END
C
C
C
      SUBROUTINE SETUPA(I)
      DOUBLE PRECISION F(100),W(100),U(100),V(100),L(100),SUMB
      DOUBLE PRECISION XF(20,100),AK(20,100),A(100,101),SUM
      COMMON/BK1/JS,F,W,U,V
      COMMON/BK3/XF,L,AK
      COMMON/BK5/A
      M1 = JS +1
      DO 10 I1 = 1, 100
         DO 5 JJ = 1, 101
            A(I1,JJ) = 0.0
    5    CONTINUE
   10 CONTINUE
C
C     FIRST ROW ELEMENTS
      A(1,1) = -V(2) - F(1) + V(1) + W(1) - (V(1) + W(1)) * AK(I,1)
      A(1,2) = V(2) * AK(I,2)
      A(1,M1) = -F(1) * XF(I,1)
C
C     LAST ROW ELEMENTS
      A(JS,JS-1) = W(JS) + V(JS) + L(JS) + U(JS) - F(JS)
      A(JS,JS) = -L(JS) - U(JS) - (W(JS) + V(JS)) * AK(I,JS)
      A(JS,M1) = -F(JS) * XF(I,JS)
C
C     MIDDLE ROW ELEMENTS
      JMINS = JS - 1
      NSTEP = 0
      SUM = 0.0
      DO 15 J1 = 2, JMINS
         SUM = SUM + F(J1-1) - W(J1-1) - U(J1-1)
         SUMB = SUM + F(J1) - W(J1) -U(J1)
         A(J1,NSTEP+1) = V(J1) + SUM - V(1)
         A(J1,NSTEP+2) = -(V(J1)+W(J1))*AK(I,J1)-U(J1)-V(J1+1)-SUMB+V(1)
         A(J1,NSTEP+3) = V(J1+1) * AK(I,J1+1)
         A(J1,M1) = -F(J1) * XF(I,J1)
         NSTEP = NSTEP + 1
   15 CONTINUE
      RETURN
      END
C
C
C
      SUBROUTINE THOMAS(I)
      DOUBLE PRECISION A(100,101),P(100),QA(100),X(20,100)
      COMMON/BK1/JS,F,W,U,V
      COMMON/BK2/X,Y,XSUM,YSUM
      COMMON/BK5/A
      M1 = JS + 1
      P(1) = A(1,2)/A(1,1)
      QA(1) = A(1,M1)/A(1,1)
      NMIN = JS - 1
      DO 5 J1 = 2, JS
```

```
      P(J1) = A(J1,J1+1) / (A(J1,J1) - A(J1,J1-1) * P(J1-1))
      QA(J1) = (A(J1,M1) - A(J1,J1-1) * QA(J1-1)) /
     1         (A(J1,J1) - A(J1,J1-1) * P(J1-1))
    5 CONTINUE
      X(I,JS) = QA(JS)
      DO 10 J1 = 1, NMIN
         JSUB = NMIN - J1 + 1
         X(I,JSUB) = QA(JSUB) - P(JSUB) * X(I,JSUB+1)
   10 CONTINUE
      RETURN
      END
```

```
15,400,1.0E-14

'LU2O3','Y2O3','YB2O3','TM2O3','ER2O3','HO2O3','DY2O3','TB2O3',
'GD2O3','EU2O3','SM2O3','ND2O3','PR2O3','CE2O3','LA2O3'

397.94,225.81,394.08,385.868,382.52,377.86,373.0,365.848,
362.50,351.92,348.70,336.48,329.814,328.24,325.82

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